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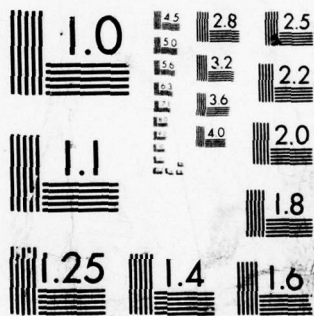
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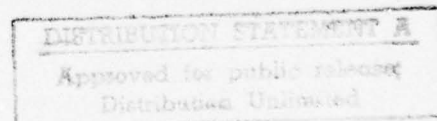
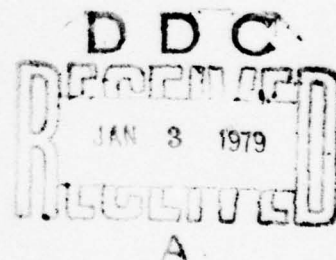
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The technical literature was reviewed in order to characterize the thermal expansion, viscosity, surface tension and wetting behavior as functions of composition for glasses of present or potential use in thick film formulations. The applicability of the principle of additivity to all properties was investigated, and good correlations were demonstrated between thermal expansion and composition in some regions of the PbO-B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> system. Experimental studies were conducted with a lead borosilicate glass as a function of Al <sub>2</sub> O <sub>3</sub> additions. The properties measured were: thermal			

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expansion from room temperature to the deformation point for both annealed and unannealed samples; viscosity from the strain point to the softening point; and initial stage sintering kinetics from which the surface tension to viscosity ratio was obtained.

## FOREWORD

Research described in this report was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907. The research was under the direction of Professor R. W. Vest. Contributing to the project were P. Palanisamy, R. L. Reed and D. Tandan.

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## I. INTRODUCTION

### A. Glasses in Thick Film Microelectronics

The purpose of this study was to characterize the chemical and physical properties of the glasses used in thick film formulations. The literature was reviewed and the physical properties of a few well characterized lead borosilicate glasses were measured. The only similar undertaking of which we are aware was a survey by Cox (1) some ten years ago. He considered the properties of commercial glasses as provided by the manufacturers, and did not feel that the actual chemical composition of the glasses was relevant. The philosophy of the present study was that physical property data had no generalized utility unless the glass composition was known.

Glass is an important constituent of all thick film components, with the possible exception of "fritless" conductives, but the total quantity of glass required by the thick film industry is infinitesimal by normal glass making standards. Because of this, there has been little inducement for the glass manufacturers to develop special glasses for microelectronics, but glass compositions developed for other applications are used in thick film formulations. For example, an inquiry to Drakenfeld Colors Division of Hercules, Incorporated solicited the following response from Robert S. Murray, Associate Director of Research and Development, "We produce a rather wide range of borosilicate lead type frits for the decorating trade on commercial glasses. Three of these frits have been picked up by the electronics trade and have been used by them for purposes somewhat unfamiliar to us." Another approach has been the development of glass compositions by the thick film industry, and the recent patent literature reveals numerous

examples of this. With either approach for obtaining glass frits for thick film formulations, it is a rare occurrence when both the composition and important physical properties of the glass are known outside of the particular company involved.

The physical properties of glasses may be varied over wide ranges by varying the composition, and the technical literature over the past 100 years abounds with examples of the adjustment of glass properties by composition variation. Unfortunately, the great majority of the glass compositions studied and reported in the open literature contain relatively high percentages of alkali metal oxides, primarily  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , which make them of only limited interest for thick film applications. This still leaves, however, a considerable body of published data on physical properties of glass compositions potentially useful in thick films, as will be discussed in Section II of this report.

Before proceeding, however, it is necessary to decide which physical properties of glass are important in their performance in various thick film components. For fritted or mixed bonded conductives, the glass phase is involved in the bonding of the conductive to the ceramic substrate, and it may be involved in the initial stage sintering of the conductive particles. To perform these functions, the glass must react chemically with the substrate and with the conductive metal. This requirement presents little or no difficulty, because molten glass is as near to a universal solvent as is known, and at the firing temperatures of thick film conductives the glass reacts with all metals and ceramics to some degree. The glass must wet and spread over the ceramic substrate and the conductive metal particles, and the rate at which this occurs depends upon the surface tension and the



viscosity of the glass; therefore, these are two properties which must be considered in any study of thick film glasses. After the high temperature reactions have occurred and the thick film conductive is cooled, the thermal contraction of the glass must be compatible with that of the ceramic substrate and the conductor to the extent that the thermal stresses developed are less than the fracture strength of the various constituents of the system. Therefore, the coefficient of linear thermal expansion is an important property of thick film glasses and has been included in the present study.

There are a few generalized requirements that can be placed on glasses for application in all thick film components (conductors, resistors, capacitors, crossovers, and cover coats). These include chemical durability, high electrical resistivity, and a low softening point relative to fused  $\text{SiO}_2$ . While other glass properties (e.g., dielectric constant) are important for other thick film components, the surface tension, viscosity, and thermal expansion which are of prime importance for thick film conductors--are also of prime importance for all other components. It must be kept in mind, however, that by virtue of carrying out its function of bonding during the high temperature firing, the composition of the glass is changed. This change in glass composition during firing means that the thermal expansion, surface tension, and viscosity of the actual glass in a thick film conductor after firing are, in general, different from these properties of the glass composition added to the conductive formulation.

#### B. The Principle of Additivity

Beginning in the latter part of the nineteenth century and continuing up to the present date, there have been efforts to find fundamentally and universally valid functional correlations between the physical properties

of glasses and their chemical composition. A recent review of the field is given by Eitel (2). Development of functional equation systems of the simplest form were always sought for these correlations. Properties such as thermal durability, modulus of elasticity, compressive and tensile strength, specific heat, specific volume, thermal expansion, viscosity, and surface tension have been represented by linear equations of the form

$$P = a_1b_1 + a_2b_2 + a_3b_3 + \dots \quad (1)$$

where P is the glass property,  $a_1$ ,  $a_2$ ,  $a_3$  etc. are weight or mole percents or fractions of the oxides, and  $b_1$ ,  $b_2$ ,  $b_3$  etc. are numerical constants. The primary difficulty with this approach is that the property-composition relations are not linear over wide composition ranges. Equation (1) can only be used within limited composition ranges wherein departures from linearity are no greater than those to be expected from measurements of a given property. Several linear equations may be needed to represent all the data in a given glass system within limits imposed by experimental errors of the property measured. Since the numerical constants  $b_1$ ,  $b_2$ ,  $b_3$  etc., vary within a given glass system, it is not surprising that they also vary for the same oxide in different glass systems.

The problems associated with applying a linear relation, such as Eq. 1, have been recognized in the technical literature for more than 80 years, and numerous attempts to solve this problem have been proposed. Most of these efforts can be divided into two categories: (1) those proposing more complex equations relating properties and composition; and (2) those which predict the composition ranges over which the linear representation will be valid. An example of the former approach is the study by Huff and Call (3),

who included terms involving the squares of oxide amounts, products of two oxide amounts, and the ratio of two oxide amounts in addition to linear terms. As input to the program, they utilized ten properties of 1400 experimental glasses. The glasses contained varying amounts of ten oxides, but they were basically  $\text{Na}_2\text{O-CaO-SiO}_2$  glasses with the other seven oxides present in relatively small amounts. The coefficients were calculated by a step-wise multiple linear-regression computer program, and the property-composition correlations on 48 soda-lime-silicate glasses not included in the data base were reasonably good. An example of the second approach, the attempts to define the composition range over which a linear equation is applicable, is the primary phase substructure method proposed by Babcock (4). This approach is based on many observations which indicate that properties are linear functions of composition within a primary crystallization phase field of the appropriate phase diagram. The application of this approach to many glass properties for a variety of glass systems is discussed in Babcock's recent book (5).

There are numerous difficulties with applying additivity to thick film glasses. The lack of an adequate data base precludes the application of methods such as Huff and Call's; it is difficult to find data on 14 compositions in a given system of interest for thick film glasses much less the 1400 utilized for the soda-lime-silicate system. It is also difficult to find sufficient data on thick film glass compositions within a given primary phase field of the appropriate ternary phase diagram. A more fundamental problem involves the degree of phase separation in glasses. Numerous studies over the past twenty years have demonstrated that metastable immiscibility and phase separation in glass systems are very common, and the degree of



phase separation is intimately related to the cooling rate. This means that glasses having the same overall composition may have a different microstructure, and hence exhibit different properties, so that factors relating composition and properties based on data collected for glasses cooled at a certain rate may not apply for the same composition glasses cooled at different rates. Since cooling rate data are hardly ever given along with composition-property data, the data base necessary for the wide-spread application of the principle of additivity to thick film glasses does not exist at this time.

### C. Scope of the Project

The literature survey was confined to thick film glasses as defined in Section IA. A glass was included in the survey only if its composition was known; this criterion eliminated many of the commercial glasses because glass manufacturers are reluctant to provide composition information on their commercial glasses. The requirement of chemical durability eliminated most of the phosphate glasses from consideration. Some glasses containing high concentrations of  $B_2O_3$  were included in the survey, even though their chemical durability is inadequate, in order to complete a series of glasses in which the properties were determined as a function of  $B_2O_3$  content with many compositions in the series having adequate chemical durability. The requirement that thick film glasses should have high electrical resistivity eliminated from consideration all glasses containing appreciable percentages of transition metal oxides. Because of the high electrical resistivity requirement, an arbitrary upper limit of 2% total alkali oxide ( $M_2O$ ) content was established; this requirement alone eliminated more than 75% of the references containing composition and property data. It was originally planned to include the

kinetics of initial stage sintering as one of the glass properties in the survey, but the only reference for a thick film glass found in the literature was our own work on one lead borosilicate composition (6).

The experimental phase of the program considered the influence of adding  $\text{Al}_2\text{O}_3$  to a lead borosilicate glass having composition by weight of 63%  $\text{PbO}$ -25%  $\text{B}_2\text{O}_3$ -12%  $\text{SiO}_2$ . This composition, which is used in some commercial thick film resistors, was chosen so as to obtain maximum benefits from the small level of effort possible under this project by conducting a few critical experiments and combining the results with data obtained on this system in prior studies (6-9) and as part of a larger on-going program in the Turner Laboratory at Purdue (10). As a result of this approach, the thermal expansion, viscosity, and surface tension were correlated with composition over a wide temperature range.



## II. LITERATURE SURVEY

### A. Sources and Selection of Data

A number of different sources were employed in order to locate publications which contained data on viscosity, thermal expansion, surface tension, contact angles, and sintering kinetics for glasses as a function of composition and temperature. The Center for Information and Numerical Data Analysis and Synthesis (CINDAS) located at Purdue University is a specialized national center for the identification, compilation, critical evaluation, analysis, and synthesis of numerical data on the physical properties of materials. Approximately 140,000 unclassified technical papers from more than 7,000 different world-wide sources are computer coded for literature searching. Properties pertinent to this project that are covered include viscosity, linear coefficient of thermal expansion, volumetric coefficient of thermal expansion, and a limited number of papers on surface tension.

A second source utilized to locate publications was the Computer-Based Information Services (CBIS) at Purdue University in conjunction with the Lockheed Information Systems. Lockheed's DIALOG is an interactive, flexible, retrieval system with natural language and assigned index search capability. It has access to more than 35 data bases with over 12 million citations/abstracts from science, technology/engineering, social sciences, and business/economics. The data base employed in this study was CA CONDENSATES (CHEMCON), which is made up of bibliographic data and key word phrases from Chemical Abstracts Service for the period 1970 to the present. The system utilizes Boolean logic to combine individual search terms through the operators OR, AND, and NOT.

The reference books listed in the Bibliography (Section VB) were consulted as data sources, and the indexes of Chemical Abstracts were utilized, with primary emphasis on the period before 1970 in order to include years not covered by CHEMCON. Key papers which were identified were studied in detail, and a list of references to prior work on topics of interest compiled. Papers on this list were then checked against references developed by all sources, and references which had not appeared from any of the other search methods were investigated.

Letters were written to 36 companies in the glass or microelectronics industries to solicit data on glasses that they manufacture or use. Of the 22 companies which responded, five provided data, but only three compositions from one of the five met the criteria for thick film glasses established in Section IA.

After narrowing the papers down to those containing data on compositions meeting the criteria in Section IA, the papers were studied in detail and if any indication was given of crystallization, that composition was eliminated from the compilation. If phase diagrams for the appropriate systems were available, these were studied and any compositions reported which were in a two liquid phase region were eliminated from the compilation.

In most instances, it was not possible to evaluate the accuracy of the data reported. If there were discrepancies observed between the same property values for the same or similar glass compositions reported by different studies, the experimental procedures described in the papers were considered and one or the other eliminated from the compilation if one technique was superior to the other. For example, softening points obtained from measuring fiber elongation in accordance with ASTM Method C338 were considered to

be more accurate than softening points inferred from DTA measurements. If it was impossible to determine the source of the variation in property values for the same composition from the information presented in the publications, both results were reported in the compilations with notes pointing out the discrepancies.

## B. Thermal Expansion

### 1. General

The thermodynamic coefficient of linear thermal expansion is defined as

$$\alpha = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_P \quad (2)$$

where the length,  $L$ , is a function of temperature at constant pressure. The thermodynamic coefficient can be calculated if an analytical equation representing the length as a function of temperature is available, or by graphically determining the slope of the length versus temperature curve at a particular temperature and dividing by the length at that temperature. The difficulty with the analytical procedure is that polynomial equations will fit the data only in limited temperature ranges. If the graphical procedure is to be used, it is more convenient to use the instantaneous coefficient of thermal expansion which will satisfactorily represent the thermodynamic coefficient under certain conditions. The instantaneous coefficient is defined as

$$\alpha_i = \lim_{T_1 \rightarrow T_2} \frac{L_2 - L_1}{L_0 (T_2 - T_1)} \quad (3)$$

where  $L_0$  is the length at some reference temperature, usually room temperature, and  $L_1$  and  $L_2$  are the lengths at temperatures  $T_1$  and  $T_2$ .



For practical applications, the mean coefficient of linear expansion between temperatures  $T_1$  and  $T_2$  is defined by

$$\bar{\alpha} = \frac{L_2 - L_1}{L_0 (T_2 - T_1)} \quad (4)$$

The mean coefficient is the quantity given in almost all data compilations for thermal expansion. An excellent review of thermal expansion with 252 references through 1968 is given by Kirby (11).

The mean coefficient is much more insensitive to changes in the expansion curve than the instantaneous coefficient, but it is definitely a function of temperature for all materials unless the length-temperature curve is a straight line. If the expansion curve is adequately represented by a quadratic equation, then the mean coefficient should be a linear function of the upper temperature. A typical expansion curve for glass is shown in Fig. 13 in Section IIID of this report. The mean coefficient increases from  $58$  to  $75 \times 10^{-7}/^{\circ}\text{C}$  as the upper temperature increases from  $100$  to  $400^{\circ}\text{C}$ , and  $\bar{\alpha}$  is a nearly linear function of the upper temperature. The rapid increase in length of the sample near  $450^{\circ}\text{C}$  is due to the temperature reaching the transformation range, and the decrease in length at still higher temperatures corresponds to viscous flow of the sample under the stress imposed by the dilatometer. The maximum in the curve is referred to as the deformation temperature.

In addition to temperature span of the measurement, the mean coefficient is also a function of the thermal history of the glass sample. A discussion of this effect along with several examples is given by Kingery et. al, (12). In general, annealed samples will have higher coefficients than samples which have not been annealed. Changes of 10% or more in the coefficient

for annealed versus unannealed samples are discussed in Section IIID of this report. The fact that the coefficient of expansion of glass samples will differ with differing prior heat treatments suggests that experimental results may also depend on the heating rate during thermal expansion measurements. The ASTM Standard Method of Test for Average Linear Expansion of Glass (C337) overcomes this difficulty because the test requires that the furnace temperature be maintained constant for at least 25 minutes or longer until the coefficients obtained from successive measurements agree to within  $0.4 \times 10^{-7}/^{\circ}\text{C}$ .

## 2. Composition Dependence

The data compilation for thermal expansion of thick film glasses is given in Appendix A. Table A1 gives data on thirty-three lead borosilicate glasses and Table A2, data on fifteen lead borosilicate glasses containing alumina. Data on thirty-one additional lead containing glasses are given in Table A3, and data on 105 lead free glasses are given in Tables A4 and A5. The deformation temperature  $T_d$  is listed whenever this reference point was quoted because it is the temperature of the maximum in the expansion temperature curve.

The applicability of the principle of additivity was investigated for the lead borosilicate glasses and the lead borosilicate glasses containing alumina because data were available for more compositions of these type glasses than any others covered in the survey. Linear regression analysis was employed to determine additivity factors for various sets of compositions; results of these studies are summarized in Table 1. Factors for both weight percent and mole percent were calculated. In the first column, all of the glass compositions in Tables A1 and A2, with the exception of

TABLE 1

## Additivity Factors for Thermal Expansion

$$\bar{\alpha} = Pw(w/o PbO) + Bw(w/o B_2O_3) + Sw(w/o SiO_2) + Aw(w/o Al_2O_3)$$

$$\bar{\alpha} = Pm(m/o PbO) + Bm(m/o B_2O_3) + Sm(m/o SiO_2) + Am(m/o Al_2O_3)$$

Glass Compositions Used (see Tables A1 and A2)						
Primary field	1-32, 34-47	34-47	1-32	1, 2, 4-7, 9-11, 13-18, 27, 36-47	20, 23, 28, 30, 45	24, 31, 32, 34, 35, 46
	Mixed	Mixed	Mixed	Tridymite	PbO · 2B <sub>2</sub> O <sub>3</sub>	PbO · SiO <sub>2</sub>
13						
$r^2$	.9821	.9827	.9830	.9967	.9988	.9999
Pw	.937 ± .033	1.004 ± .097	.914 ± .038	.735 ± .027	.958 ± .147	2.236 ± .210
Bw	.711 ± .099	.769 ± .221	.707 ± .112	.797 ± .044	.333 ± .409	-7.806 ± 1.830
Sw	-.010 ± .948	-.060 ± .113	.018 ± .054	.055 ± .020	-.021 ± .596	.396 ± .325
Aw	.342 ± .475	-.089 ± 1.299	-0-	-.086 ± .230	.396 ± 1.033	.299 ± .394
$\sigma$ (10 <sup>-7</sup> /°C)	8.1	8.8	7.9	2.5	3.8	1.7
$\Delta\bar{\alpha}$ (Glass No. 33)	5.7	10.8	4.5	-4.1	-2.6	-120.5
$\Delta\bar{\alpha}$ (Glass No. 48)	7.0	10.2	-	-4.1	-0.7	-114.3
$\Delta\bar{\alpha}$ (Glass No. 49)	9.3	10.6	-	-3.1	2.2	-107.1
$r^2$	.9892	.9839	.9878	.9963	.9977	.9999
Pm	1.362 ± .051	1.455 ± .095	1.339 ± .066	1.282 ± .071	1.163 ± .264	2.844 ± .351
Bm	.596 ± .062	.691 ± .102	.578 ± .077	.762 ± .041	.476 ± .231	-3.072 ± .958
Sm	.178 ± .027	.145 ± .043	.196 ± .033	.126 ± .018	.387 ± .275	.403 ± .147
Am	.036 ± .322	-.500 ± .525	-0-	-.110 ± .315	.447 ± .908	.522 ± .304
$\sigma$ (10 <sup>-7</sup> /°C)	6.3	5.2	6.7	2.7	3.8	1.9
$\Delta\bar{\alpha}$ (Glass No. 33)	4.3	10.7	3.2	7.5	-2.5	-97.3
$\Delta\bar{\alpha}$ (Glass No. 48)	4.0	7.7	-	6.4	-0.6	-90.5
$\Delta\bar{\alpha}$ (Glass No. 49)	4.8	5.7	-	6.4	2.4	-83.0



the results of the present study (Glass Nos. 33, 48 and 49), were utilized in the linear regression analysis. These 45 glass compositions when entered into the program as weight percents gave a coefficient of determination ( $r^2$ ) of .9821, the four factors with their standard deviations listed in Table 1, and a standard deviation ( $\sigma$ ) of  $8.1 \times 10^{-7}/^\circ\text{C}$ . The fit of the data when calculated as mole percents is slightly better as evidenced by an  $r^2$  value closer to 1 and a smaller  $\sigma$ , but the standard deviation is still 11% of the mean value of all the coefficients in Tables A1 and A2. The differences between measured and calculated mean coefficients ( $\Delta\bar{\alpha}$ ) for the three glass compositions measured in this study are also slightly less when using the mole percent factors, and represent a 6-8% error which is within the possible experimental error. Column 2 of Table 1 gives the results of the linear regression analysis utilizing only glass compositions 34-47, which are compositions containing all four of the ingredients of interest. The statistical parameters ( $r^2$  and  $\sigma$ ) are similar to those found for the compositions in column 1, but the fit to the three experimental glasses is not as good. Column 3 of Table 1 represents the results of the linear regression analysis on the lead borosilicate glass compositions 1-32 of Table A1, and the statistical parameters are seen to be similar to those found for the glass compositions used to generate the results in columns 1 and 2. Only experimental glass No. 33 could be used for comparison of measured and calculated coefficients because the other two experimental glasses contained  $\text{Al}_2\text{O}_3$ . The fit on a weight percent or a mole percent basis (6% and 5% respectively) is within the anticipated experimental error.

The last three columns in Table 1 represent compositions chosen so that they would all lie within the same primary phase field of the

PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram (13). According to Babcock's primary phase substructure method (3, 4), the principle of additivity should hold, on a mole percent basis, for compositions all lying within the same primary phase field. The 28 compositions used in the linear regression analysis to obtain the results given in column 4 of Table 1 all were within the tridymite primary field. The coefficient of determination and standard deviation indicate a good fit on either a weight percent or mole percent basis, and the standard deviations on the factors for PbO, B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are relatively small. The fit to the measured coefficients of the three experimental glasses is no better than where all compositions were included (column 1), but the experimental glass compositions do not fall in the tridymite phase field so there is no reason to expect a good fit. The last two columns of Table 1 are compositions lying within the PbO·2B<sub>2</sub>O<sub>3</sub> and PbO·SiO<sub>2</sub> primary phase fields, respectively. Correlation coefficients and standard deviations are very good, but this is primarily due to the fact that the number of compositions is small; the standard deviations on the factors are seen to be quite large. The experimental glass compositions fall within the PbO·2B<sub>2</sub>O<sub>3</sub> primary field, and the differences between the measured and calculated coefficients of thermal expansion given in column 5 are the smallest of any of the six data sets.

Results shown in Table 1 tend to support Babcock's contention that the principle of additivity can be applied for thermal expansion for compositions within a given primary phase field, but the fit is reasonably good for glass compositions in several primary fields. A variation of  $\pm 10\%$  in the mean coefficient of thermal expansion is the best that can be expected due to the variations in measurement techniques and thermal history discussed in part 1 of this section.



## C. Viscosity

### 1. General

When a mechanical stress is applied to glass, deformation occurs by a viscous flow mechanism. Under almost all conditions for thick film glasses the deformation may be described as Newtonian, i.e., the strain rate is directly proportional to the applied stress and the viscosity is a function of temperature only. An excellent review of both experimental and theoretical aspects of glass viscosity is given in Volume VII of Silicate Science (14).

For molten glasses, the viscosities of interest range from  $10$  to  $10^{14}$  Pa·s\*. There are numerous reference temperatures corresponding to viscosities within the range  $10$ - $10^{14}$  Pa·s which are important in various areas of glass manufacturing and processing. Six of these reference points which are defined and discussed in the ASTM Standards (15) are listed in Table 2. Other reference points which have been mentioned in the literature include: the flow point which corresponds to a viscosity of  $10^4$  Pa·s (16); the intrusion point or penetration point which correspond to a viscosity of  $10^3$  Pa·s (17); the setting point which is variously defined as  $5^\circ\text{C}$  above the strain point or  $15^\circ\text{C}$  below the annealing point (1); the sag point (18); and several others (19). One of the reasons for the large number of reference points introduced by various researchers are attempts to describe the temperature dependence of the viscosity, as discussed later.

In order to interpolate and extrapolate viscosity measurements, it is desirable to have an analytical expression for the temperature dependence of viscosity. The most widely used expression is an empirical equation

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\* A Pascal second (Pa·s) is the SI unit for viscosity. Almost all of the technical literature is in the CGS unit of poise: 1 Pa·s is equal to 10 poise.

TABLE 2  
Viscosity Reference Points for Glass

Viscosity (Pa·s)	Reference Point	Remarks
10	Melting ( $T_m$ )	For melting at a commercially desirable rate the viscosity should be 100.5 to 101.5 Pa·s. The temperature for which the viscosity is 10 Pa·s is used for comparing glasses.
$10^3$	Working ( $T_w$ )	The working temperature is the upper end of the working range which extends from a viscosity of $10^{6.6}$ to $10^3$ Pa·s.
$10^{6.6}$	Softening ( $T_s$ )	The softening point is the temperature at which a fiber elongation rate of 1mm/min is measured by ASTM Method C-338. For a glass with specific gravity near 2.5, $T_s$ corresponds to a viscosity of $10^{6.6}$ Pa·s.
$10^{10.5}$	Deformation ( $T_d$ )	The deformation point corresponds to the temperature where viscous flow counteracts the expansion measured by the interferometer method. The viscosity at $T_d$ is $10^{10}$ to $10^{11}$ Pa·s.
$10^{12}$	Annealing ( $T_a$ )	The annealing point is the temperature at which a fiber elongation rate of 0.0136 cm/min is measured by ASTM Method C-336. Internal strains will be relieved in about 15 minutes at $T_a$ , and the viscosity is approximately $10^{12}$ Pa·s.
$10^{13.5}$	Strain ( $T_{st}$ )	The strain point is the temperature at which a fiber elongation rate of 0.00043 cm/min is measured by ASTM Method C-336. Internal strains will be relieved in about 4 hours at $T_{st}$ , and the viscosity is approximately $10^{13.5}$ Pa·s.

proposed by Fulcher (20),

$$\log \eta = A + B/(T - T_0) \quad (5)$$

in which  $\eta$  is the viscosity and A, B and  $T_0$  are arbitrary constants. Extensive measurements carried out on two standard glasses by NBS and several other participating laboratories have shown that the Fulcher equation fits the viscosity of these glasses within experimental accuracy between 10 and  $10^{11}$  Pa·s (21). In view of the great empirical success of the Fulcher equation, many different theoretical models have been proposed to account for it, but all of the models require arbitrary approximations to reduce the theoretical equation to the form of the Fulcher equation (21, 22). At the present time the Fulcher equation must be accepted as a purely empirical expression and the constants A, B and  $T_0$  are truly arbitrary constants with no physical significance.

An alternate approach to describing the temperature dependence of the viscosity is to use the two parameter Arrhenius equation,

$$\eta = A \exp (Q/RT) \quad (6)$$

over a limited temperature range. This approach (23) is based on the theory that the viscosity-temperature curves are subdivided in "critical zones" between which Eq. 6 applies, the discontinuities ("critical points") being caused by changes in the activation energy brought about by changes in bonding conditions between clusters of atoms. The simplest approach would require only three zones defined by two critical points, but the larger the number of zones the better the fit to any set of experimental data; this is one of the reasons for the proliferation of critical points discussed above.

## 2. Composition Dependence

The viscosity data for thick film glasses that resulted from this survey are tabulated in Appendix B. Thirty-five glass compositions containing lead are given in Table B1, and 17 lead free glasses are listed in Table B2. Nine reference temperatures corresponding to viscosities from  $10$  to  $10^{13.5}$  Pa·s are given for these glass compositions. The only compositions included in Tables B1 and B2 were those for which data for at least three of the nine reference point viscosities were reported.

The viscosity of oxide glass melts is a strong function of composition. For silicate glass melts, viscosity is almost always found to decrease with increasing concentration of modifying cations, while the addition of alumina usually increases it. The principle of additivity has been applied to the viscosity of various alkali containing commercial glasses by calculating the one or more of the critical temperatures given in Tables B1 and B2. For example, factors to give temperatures corresponding to viscosities of  $10$ ,  $10^2$ ,  $10^4$ , and  $10^6$  Pa·s are given by Babcock (4) for three different compositional regions of the  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system and for all glasses combined into one group. Maximum differences between measured and calculated temperatures for combined groups were, in all cases, two times as large as those in separate phase groups, which suggests that the primary phase substructure method is useful in defining the range of compositions over which linear additivity can be applied to viscosity. It is unfortunate that there is not a sufficient amount of data available for alkali free glass compositions to evaluate the applicability of the principle of additivity to glasses of interest for thick film applications.



As near as can be determined, all of the data in Appendix B were collected in air, but the relative humidity was rarely specified. This is unfortunate because the viscosity of silica (24), silicate glasses (25), and lead borosilicate glasses (26) have been shown to decrease with increasing partial pressures of water vapor. This is apparently due to water vapor entering the glass through the formation of hydroxyl groups (25), the concentration of which depend on the square root of the water vapor partial pressure. The effect of water vapor on viscosity persists even to very high temperatures (27).

Also included in Appendix B is a copy of the paper by Abou-El-Azm and El-Batal (28) which lists the softening points for over 300 glass compositions, many of which are of potential interest in thick film microelectronics. The reported values are Littleton softening points which should correspond to a viscosity of  $10^{6.6}$  Pa·s, but there are discrepancies between the softening points reported in this paper and those reported by other investigators for every case where comparisons can be made. For example, a lead silicate glass with 70.39 mole percent PbO is reported to have a softening point of 588°C, whereas a lead silicate glass with 70 mole percent PbO (Glass No. 19 in Table B1 from reference B5) has a reported softening point of 427°C. The experimental techniques employed in the two papers, while different, both appear to be valid, and a difference of 161°C in the softening point is well beyond any expected experimental error. Another comparison can be made with Glass No. 3 of Table B1, a lead borate with a reported softening point of 330°C; Abou-El-Azm and El-Batal report this same composition to have a softening point of 461°C, a discrepancy of 131°C. If the compositions reported by Abou-El-Azm and El-Batal were in fact weight percent

instead of mole percent as they indicate, the agreement between their results and other published results are much closer where comparisons can be made. For example, Glass No. 8 of Table B1 is a lead silicate with 65 weight percent PbO and a reported softening point of 632<sup>0</sup>C; Abou-El-Azm and El-Batal give 627<sup>0</sup>C for the softening point of a lead silicate with 65.01% PbO. Accordingly, the column headings in the paper by Abou-El-Azm and El-Batal in Appendix B have been changed to read wt.%.

#### D. Surface Tension

##### 1. General

The surface tension of a material is the force required to extend the surface a unit length, but since a liquid (glass) cannot support shear stresses, its surface tension is equal to its surface energy, which is the work required to increase the surface by unit area. The surface energy is actually an interfacial energy between the liquid and vapor phases, which means that the nature of the vapor phase will influence surface tension values. Therefore, the composition of the vapor phase must be characterized as well as the composition of the glass. Most of the experimental studies involving surface tension of glasses have been conducted in air, but the relative humidity has rarely been specified. This is unfortunate because water vapor is an important constituent of the vapor phase. For example, studies of soda-lime silicate glasses (29) showed that the surface tension-to-viscosity ratio, as calculated from initial stage sintering data, changed by more than a factor 10 as the partial pressure of water vapor in the atmosphere changed from 0.61 to 54 kPa. It has also been shown (30) that the surface tension of a soda-lime-silica glass is decreased in proportion to the square root of the partial pressure of water vapor at low partial pressures.

"Soluble gases" such as  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{SO}_3$ , which react with the glass melt, have even larger effects on surface tension values than do water vapor (31).

Since the surface tension is a surface free energy, a first order approximation for the temperature dependence would be a small, linear, negative temperature dependence with the coefficient representing the surface entropy. This general tendency is observed with the temperature coefficients usually being small (e.g., 0.01 to 0.07  $\text{mN/m}^\circ\text{C}^*$ ) and negative, but positive temperature coefficients of surface tension have been observed for numerous glass systems. Part of the variation in observed temperature dependences may be associated with surface segregation as originally suggested by Worley (32). The system can minimize its surface energy if constituents of the glass which tend to lower to surface tension concentrate in the surface layer, and constituents which tend to increase the surface tension concentrate in the bulk. The segregation will continue until the concentration gradients produced balance the driving force of surface energy reduction, and the concentration gradients so produced will vary with temperature. It is the system's attempt to minimize its free energy by changing compositions of the surface layer that lead to positive and negative temperature dependences, and to highly nonlinear composition-surface tension effects.

The surface tension value obtained on a glass appears to be a function of the time for which the glass is maintained at elevated temperatures. Shartsis and Smock (33) found that the surface tension values for some

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\* The SI unit for surface tension is newton per meter (N/m) whereas almost all of the technical literature gives surface tension in dynes per centimeter. Fortunately,  $1 \text{ mN/m} = 1 \text{ dyne/cm}$ .



glass compositions would increase approximately 3% during the first 20-40 hours at temperature and then become constant, while other glass compositions had surface tensions which were still increasing after 100 hours at temperature. This effect is probably due to the selective volatilization of one constituent from the glass, but definitive studies of this time effect were not found in the literature.

## 2. Composition Dependence

Surface tension data on thick film glasses are presented in Appendix C. Table C1 gives data on 51 lead containing glasses, primarily binary lead borates or lead silicates. Table C2 gives data on 159 lead free glasses, approximately 90% of which are barium borosilicates. The surface segregation effects are clearly demonstrated in the  $\text{PbO-B}_2\text{O}_3$  system (Glass Nos. 1 through 23 in Table C1). As the amount of  $\text{PbO}$  relative to  $\text{B}_2\text{O}_3$  is increased from 0 to 40 weight percent, the surface tension at  $800^\circ\text{C}$  remains constant (Glass Nos. 1-9 in Table C1); the surface of the glass is still nearly pure  $\text{B}_2\text{O}_3$  even when the overall composition contains 40%  $\text{PbO}$ . As still more lead oxide is added, the surface tension does begin to increase and the temperature coefficient, which had remained positive and constant, becomes more negative.

A similar surface segregation effect is observed for the  $\text{BaO-B}_2\text{O}_3$  system, but it is not as pronounced. A consideration of Glass Nos. 54 through 70 in Table C2 shows that the surface tension at  $900^\circ\text{C}$  has a value of approximately 80, characteristic of pure  $\text{B}_2\text{O}_3$ , until the composition is somewhere between 15 and 25 weight percent  $\text{BaO}$  at which point it begins to increase. This indicates that the surface is essentially pure  $\text{B}_2\text{O}_3$  until approximately 10 mole percent  $\text{BaO}$  is added as opposed to approximately 20 mole percent  $\text{PbO}$ .



Babcock (5) used data on 28 of the BaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses listed as Glass Nos. 76 through 172 in Table C2 selected to have compositions within the 3BaO·3B<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> primary phase field. Compositions were converted to mole fractions, and the data were subjected to a linear regression analysis with the following results for surface tension at the four indicated temperatures:

$$\gamma = 263.99X_s + 93.52X_B + 423.12X_{Ba} \quad (1300^\circ\text{C})$$

$$\gamma = 254.82X_s + 90.83X_B + 444.45X_{Ba} \quad (1200^\circ\text{C})$$

$$\gamma = 247.76X_s + 88.91X_B + 463.57X_{Ba} \quad (1100^\circ\text{C})$$

$$\gamma = 251.30X_s + 94.02X_B + 468.92X_{Ba} \quad (1000^\circ\text{C})$$

In these equations  $X_s$ ,  $X_B$  and  $X_{Ba}$  are mole fractions of SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and BaO, respectively. Differences between measured and calculated values of surface tension at the four temperatures were 1.2, 0.9, 0.9, and 1.2 mN/m, respectively.

#### E. Wetting Behavior

The wetting of a non-deformable solid surface by a glass is commonly represented analytically by Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (7)$$

where  $\gamma_{sv}$  is the solid-vapor interfacial energy,  $\gamma_{sl}$  is the solid-liquid interfacial energy,  $\gamma_{lv}$  is the liquid-vapor interfacial energy (the surface tension of the glass), and  $\theta$  is the contact angle measured through the liquid phase. It is also common to refer to non-wetting as the behavior for values of theta greater than 90°, and wetting for values of theta less than 90°;  $\theta = 0$  represents complete wetting or spreading. The driving

force for spreading is often represented by a spreading coefficient,  $S$ , given by:

$$S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \quad (8)$$

Two necessary conditions for the applicability of Young's equation are: (1) the effect of adsorbed layers on the surface energies at the time of test must be known; and (2) no interfacial compounds which form a distinct third-phase may be formed (34). The solid-vapor interfacial energy is a direct function of the composition of the vapor phase as well as the composition of the solid. The surface energies (surface tensions) of thick film glasses were discussed in the preceding section, and these values were found to depend on the composition of the vapor phase in addition to composition of the glass. The solid-liquid interfacial energy will depend on the surface composition of the solid at the time of wetting, which is a function of the composition of the vapor phase and the temperature prior to wetting. Therefore, all three interfacial energies in Young's equation are functions of the partial pressures of all species in the gas phase, but the exact dependence is not known for a single system. Even if the second necessary condition for applicability of Young's equation is satisfied, wetting cannot be predicted because of the uncertainty in the interfacial energies. The extensive work by Pask and co-workers (35) has greatly contributed to an overall understanding, but no consistent theory explains wetting in all inorganic systems.

One of the difficulties in interpreting wetting studies is that the phases of the solid-liquid-vapor system may not be at chemical equilibrium prior to the experiment. Under non-equilibrium conditions, the effect of

chemical reactions on the interfacial tensions has to be considered. In order for wetting to occur, there must be some degree of chemical interaction between the glass and solid surface, and the composition of the glass will change to some extent during the wetting process. Because of this interaction, it is sometimes convenient to consider initial contact angles and final contact angles (or initial and final spreading coefficients) for the pure phases and the mutually saturated phases, respectively. For example, a study (36) of the wetting of platinum by a low alkali calcium-alumino-borosilicate glass at  $1030^{\circ}\text{C}$  gave an initial contact angle of  $88^{\circ}$  which decreased rapidly after a few minutes and arrived asymptotically at an equilibrium value of  $20^{\circ}$  after about 30 minutes. At  $1155^{\circ}\text{C}$ , the initial contact angle was  $25^{\circ}$  and decreased to  $10^{\circ}$  after 10 minutes, but then began increasing and reached an equilibrium value of  $18^{\circ}$  after 30 minutes. This increase in contact angle involved a corresponding retraction or dewetting of the glass. At  $1400^{\circ}\text{C}$  for the same system, the dewetting phenomena was even more pronounced: the contact angle, initially  $22^{\circ}$ , increased very rapidly to over  $40^{\circ}$  after 10 minutes, and then decreased slightly to its equilibrium value of  $38^{\circ}$  after an additional 10 minutes. However, if the same system was initially brought to equilibrium at  $1400^{\circ}\text{C}$  and then the temperature lowered with sufficient time allowed at each temperature for the glass to assume its new equilibrium contact angle, a temperature independent contact angle of approximately  $38^{\circ}$  was observed with no tendency for dewetting even when the temperature was lowered below  $1000^{\circ}\text{C}$ . These results indicate that it is even risky to talk of initial and final contact angles because of the lack of reversibility.



The differences in the contact angle at which a glass advances over a solid surface, and the angle with which the glass recedes from a previously wetted surface may be due to an adsorbed layer initially on the solid surface which is dissolved in the glass on initial wetting, but it may also be due to irreversible changes in the solid surface after wetting. Considerations of the thermodynamics of a solid-liquid-vapor system under chemical non-equilibrium conditions (37) showed that mass transfer across an interface results in a transient decrease in the corresponding specific interfacial free energy and the interfacial tension by an amount equal to the free energy of the effective chemical reaction per area at that interface. When the reaction is between the solid and the liquid, this transient lowering of the interfacial tension can cause the liquid to spread on the solid surface if the interfacial energy reduction is large enough, and also if the diffusion rates of the reacting components in the solid phase are slow enough relative to the flow rate of the liquid to cause the liquid at the periphery of the drop to be in dynamic contact with unreacted solids.

Rather than equilibrium contact angles, it is perhaps more appropriate to consider the kinetics of spreading. The case of a liquid droplet on a flat and rigid solid surface was discussed by Yin (38) based on the assumption that spreading is impelled by the horizontal components of the surface tension at the 3-phase boundary and retarded by the viscous flow of the droplet. This work showed that the instantaneous rate of spreading in terms of area per unit time is

$$\frac{dA}{dt} = \left(\frac{4\pi}{\eta}\right) \left(\frac{3V_0}{\pi}\right)^{1/3} (SI_1 + \gamma I_2) \quad (9)$$



where  $\eta$  is the viscosity of the liquid,  $V_0$  is the volume of the droplet,  $\gamma$  is the surface tension,  $S$  is the spreading coefficient, and  $I_1$  and  $I_2$  are definite integrals as functions of the instantaneous contact angle only. The dependence of viscosity leads to the conclusion that lowering of the contact angle or spreading may not necessarily be observed during an interfacial reaction if the viscosity of the liquid is too high.

There is a considerable amount of data in the literature on contact angles of glasses on various metals and ceramics, but the overwhelming majority of the glasses are high alkali content because of their commercial importance. A considerable amount of data is available on contact angles of E-glass on various noble metals (36, 39). The E-glass is a commercially available calcium-alumino-borosilicate glass manufactured by Pilkington Brothers Ltd., but its exact composition is not known so it was not included in the compilation. The only significant amount of data discovered on what could be considered thick film glasses was from the work at RCA with Drakenfeld E1527 glass, which is a lead borosilicate with a small amount of other oxides as indicated in Appendix D. Contact angles were reported for this glass on alumina, copper, silver, and gold substrates, and for this base glass with 30 weight percent  $\text{Bi}_2\text{O}_3$  oxide added on alumina and gold substrates.

### III. EXPERIMENTAL STUDIES

#### A. Glass Compositions and Preparation

Glass melts were prepared by mixing appropriate quantities of  $\text{Pb}_3\text{O}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in a rolling jar. The mixed powders were transferred to a platinum crucible, heated to the firing temperature (950 to 1050°C depending on the amount of  $\text{Al}_2\text{O}_3$  in the melt) and mixed at temperature with a platinum stirrer for ninety minutes. In order to prepare samples for the sintering studies, the glass melts were fritted in deionized water, ground in an agate ball mill, and separated into particle size fractions utilizing standard sieves. The sieve fraction between 175 and 230  $\mu\text{m}$  was used for making spheres in a two-section vertical tube furnace with the lower section maintained at 800°C and the upper section at 1200°C. Glass particles were fed into the top of the furnace utilizing a vibrating sieve and they became spherical in order to minimize their surface energy as they travelled through the furnace. The spheres were collected in vacuum pump oil at the bottom of the furnace and cleaned with trichoroethylene and acetone. Samples for viscosity and thermal expansion measurements were prepared by pouring the glass melt at approximately 800°C into steel molds preheated at 250°C in order to reduce thermal shock. Specimens which were to be tested in an unannealed condition were immediately removed from the mold and cooled to room temperature in air. The samples which were to be annealed were placed in a furnace at approximately 50°C and the temperature was raised to the annealing point (440°C to 460°C depending upon the glass composition). The annealing temperature was maintained for one half hour and then the samples were cooled at approximately 3° per minute to

100°C. The appropriate size specimens were then cut using a diamond saw.

## B. Viscosity

### 1. Apparatus and Procedure

Trouton (40) was the first researcher to derive an expression for the viscous traction of horizontally supported beams. Experimental techniques for determining viscosities in the range of  $10^7$  to  $10^{14}$  Pa·s by measuring beam bending were described by Hagy (41). A modified form of Hagy's expression for the viscosity of a centrally loaded beam in terms of its mid-point deflection rate is:

$$\eta = (g\ell^3/144I_c v) \left[ L + (\rho_g A\ell/1.6) \right] \quad (10)$$

In this equation:

$g$  = acceleration due to gravity

$\ell$  = free span length

$I_c$  = cross sectional moment of inertia (width x thickness<sup>3</sup>/12)

$v$  = mid-point deflection rate

$L$  = load

$\rho_g$  = glass density

$A$  = cross sectional area

A schematic diagram of the beam bending viscometer developed to measure the mid-point deflection,  $v$ , of a glass beam as a function of time at elevated temperatures is shown in Fig. 1. The viscometer assembly was housed in a clam shell tube furnace 10 cm in diameter with a heated length of 60 cm. The furnace was mounted on a wheeled support so that it could be moved independent of the viscometer assembly. The furnace temperature

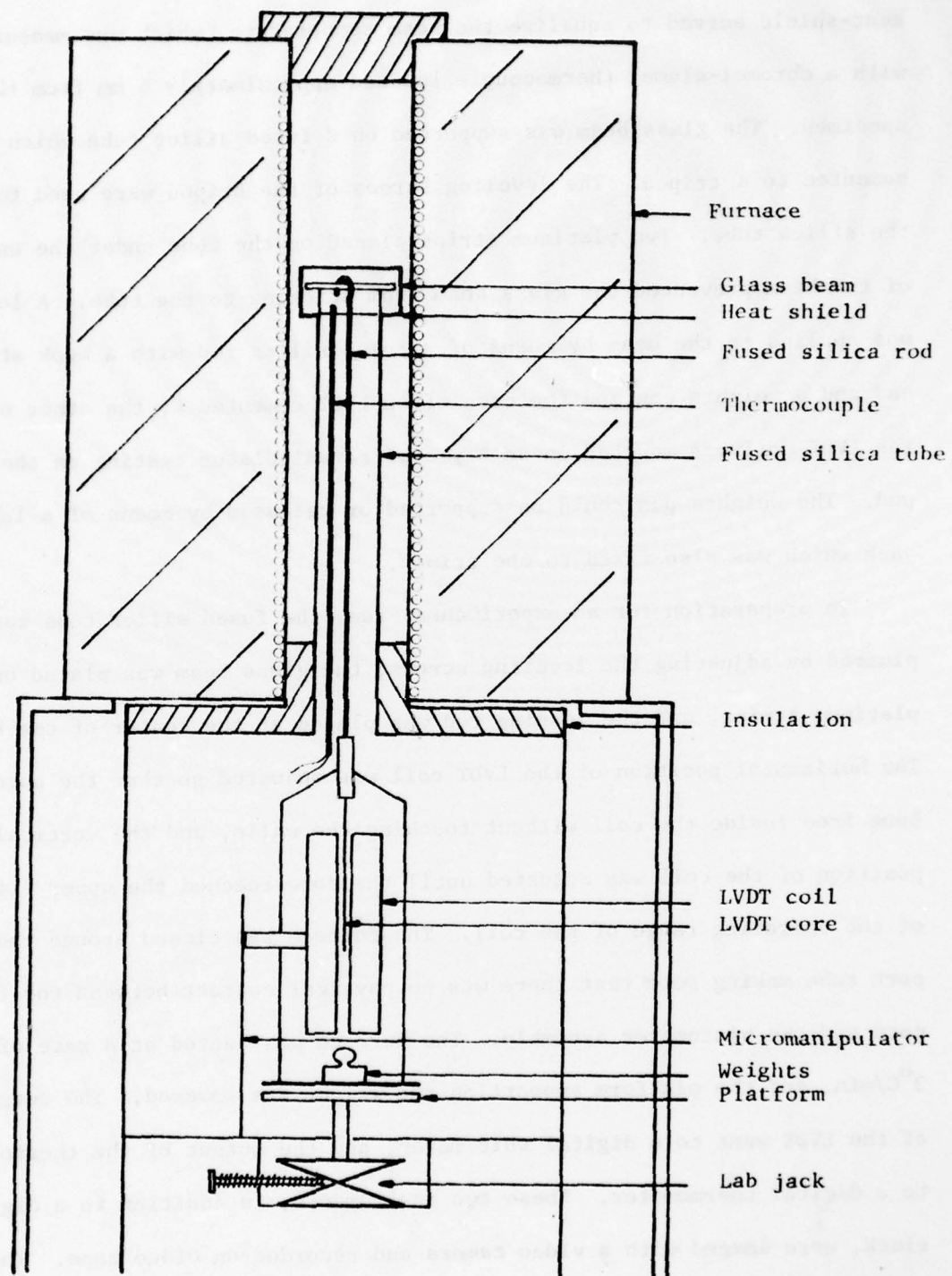


Figure 1. Beam Bending Viscometer



was controlled by an SCR programmable controller. The stainless steel heat-shield served to equalize the beam temperature, which was measured with a chromel-alumel thermocouple located approximately 5 mm from the specimen. The glass beam was supported on a fused silica tube which was cemented to a tripod. The leveling screws of the tripod were used to plumb the silica tube. Two platinum strips placed on the tube under the ends of the beam prevented the glass beam from sticking to the tube. A load was applied to the beam by means of a fused silica rod with a hook at one end and a weights pan and the core of an LVDT cemented to the other end. The LVDT coil was mounted on an x-y-z micromanipulator resting on the tripod. The weights pan could be supported or released by means of a lab jack which was also fixed to the tripod.

In preparation for an experimental run, the fused silica tube was plumbed by adjusting the leveling screws, the glass beam was placed on the platinum strips, and the loading rod was placed at the center of the beam. The horizontal position of the LVDT coil was adjusted so that the core hung free inside the coil without touching the walls, and the vertical position of the coil was adjusted until the core reached the upper limit of the operating range of the coil. The furnace was closed around the support tube making sure that there was no physical contact between the furnace and the viscometer assembly. The furnace was heated at a rate of  $3^{\circ}\text{C}/\text{min}$ , and the platform supporting the weight was lowered. The output of the LVDT went to a digital volt meter, and the output of the thermocouple to a digital thermometer. These two instruments, in addition to a digital clock, were imaged with a video camera and recorded on video tape. This procedure was followed because all three variables (deflection, time, and

temperature) had to be simultaneously recorded, and the video camera was available and provided a convenient means to accomplish this.

The linearity of the system was investigated by measuring the deflection of a beam at constant temperature; the results of this experiment are shown in Fig. 2. The deflection rate (the slope of the line) is seen to be quite constant, and this rate,  $v$ , when substituted in Eq. 10 along with the beam constants, gives the viscosity. After it was established that the mid-point deflection was a linear function of time at constant temperature, the program controller was used to increase the beam temperature at a rate of approximately  $3^{\circ}\text{C}/\text{min}$ , and the video tape record used to determine the change in deflection over a 20 second time span during which the temperature would change less than  $1^{\circ}\text{C}$ . Typical results for mid-point deflection as a function of time under increasing temperature conditions are shown in Fig. 3.

The stability of the viscometer assembly was checked by replacing the glass beam with a thick fused silica rod, and the system was found to be stable even at  $600^{\circ}\text{C}$ , i.e., no apparent beam deflection was measured. The reliability of the viscometer and the experimental technique was evaluated by using Viscosity Standard No. 711 supplied by the National Bureau of Standards. This was a lead silicate glass composition for which the viscosity has been precisely established by several laboratories. Figure 4 shows our results for this glass along with the values predicted by NBS; the agreement is seen to be very good.

## 2. Results and Discussion

The viscosities obtained for the standard glass (63w/o  $\text{PbO}$ -25w/o  $\text{B}_2\text{O}_3$ -12w/o  $\text{SiO}_2$ ) and the standard glass with 8 weight percent dissolved alumina

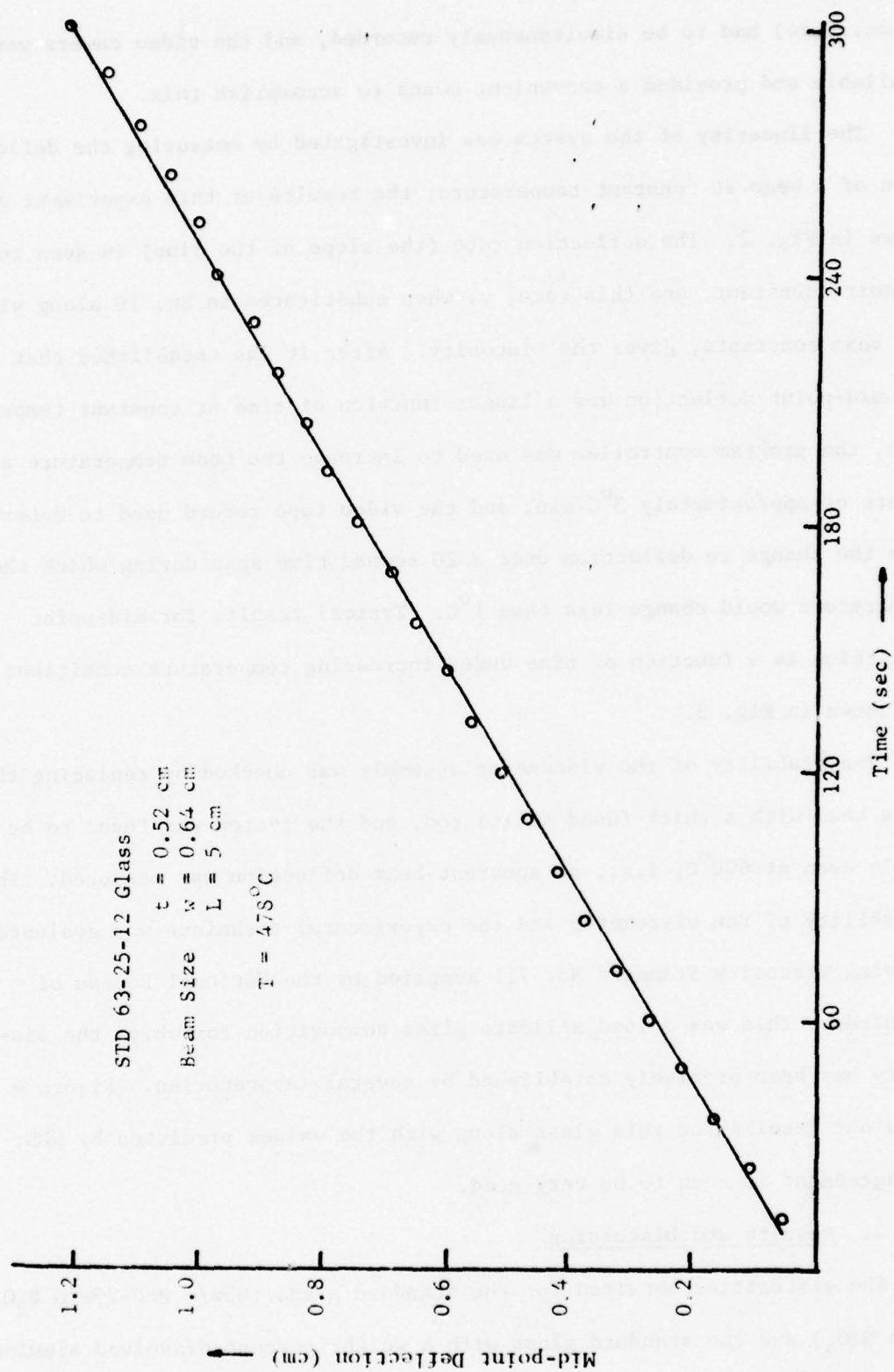


Figure 2. Isothermal Mid-point Deflection of Glass Beam.

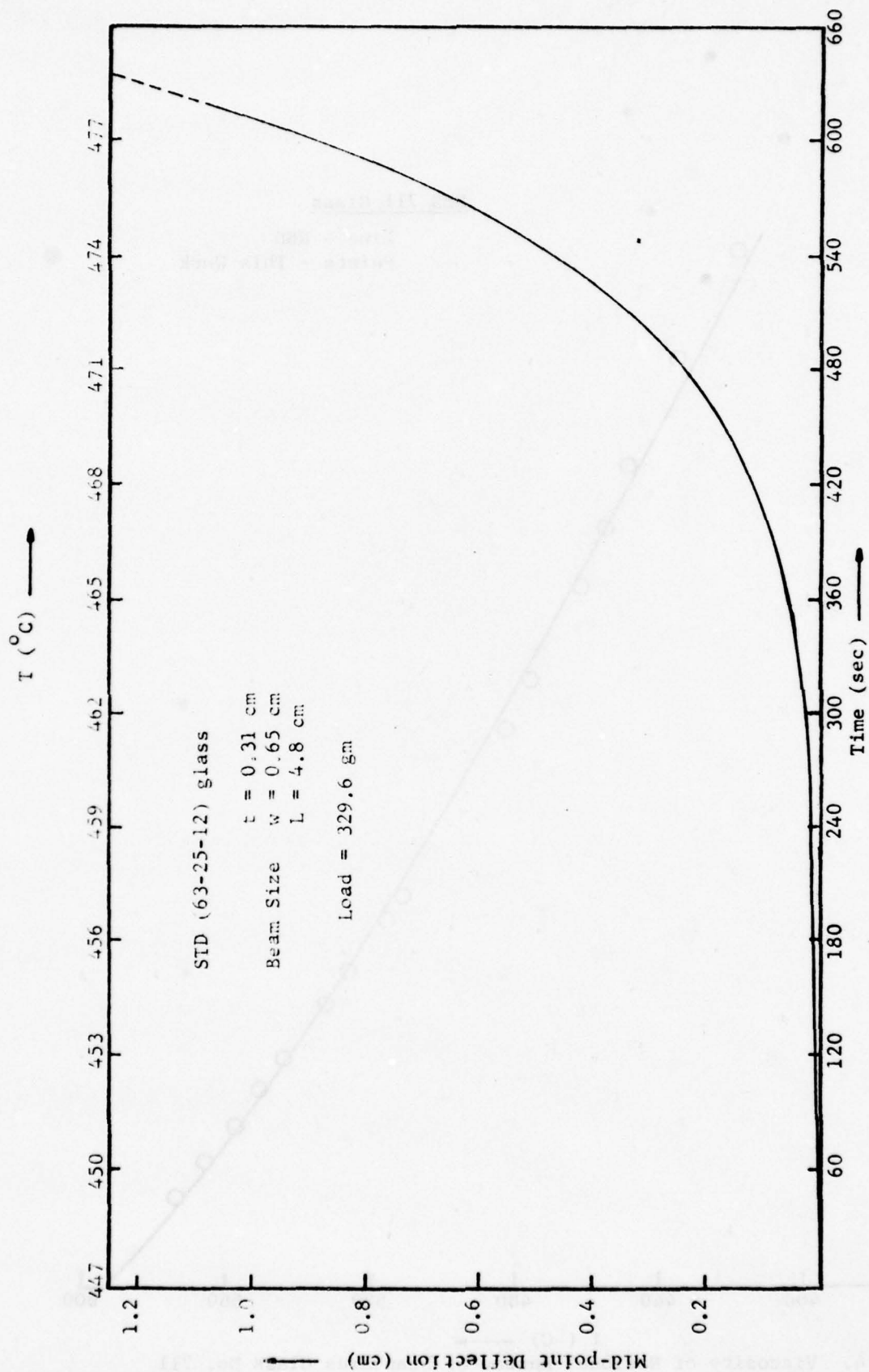


Figure 3. Constant Heating Rate Mid-point Deflection of Glass Beam.



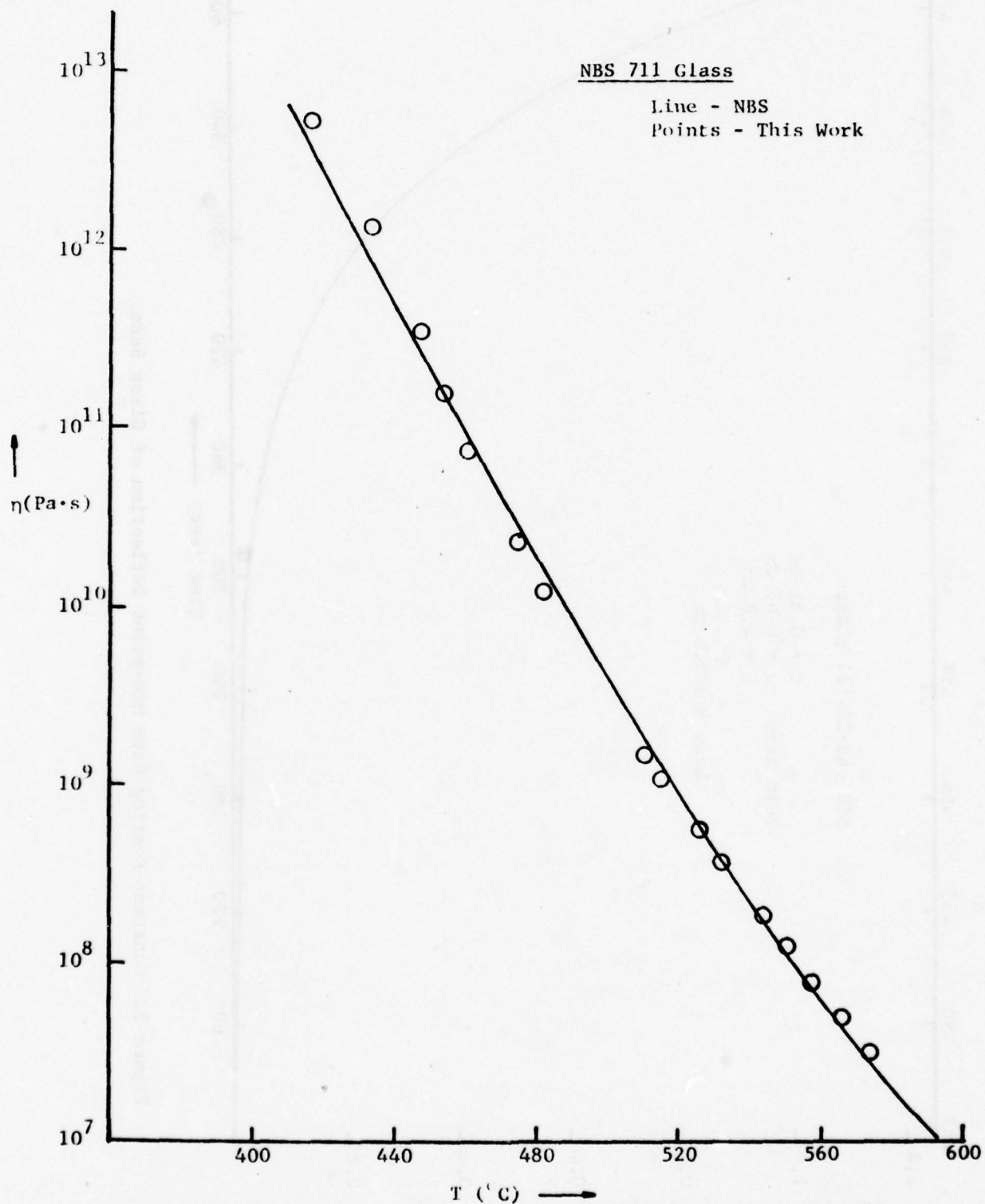


Figure 4. Viscosity of National Bureau of Standards Glass No. 711

(58w/o PbO-23w/o B<sub>2</sub>O<sub>3</sub>-11w/1 SiO<sub>2</sub>-8w/o Al<sub>2</sub>O<sub>3</sub>) are shown in Figs. 5 and 6. These data span the temperature range from near the softening point ( $\eta = 10^{6.6}$  Pa.s) to the annealing point ( $\eta = 10^{12}$  Pa.s) for each of the glasses. Figure 7 is an Arrhenius plot of viscosity data for six glass compositions fabricated and measured for another research project (10). The curve labeled "STD" is a replot of the data for the 63-25-12 glass shown in Fig. 5. The other five curves are data for the 63-25-12 glass with 2, 4, 6, 8 and 10 weight percent dissolved AlSiMag 614\*, a nominal 96% alumina ceramic with the composition given in Table 3. The viscosity data for the 58-23-11-8 glass (Fig. 6) when replotted as log  $\eta$  versus reciprocal temperature will give a curve almost identical to the 6% curve of Fig. 7, particularly at higher temperatures. This means that 8 weight percent pure alumina is required to have the same effect on viscosity as 6 weight percent of the ceramic composition given in Table 3.

All of the glass compositions in Fig. 7 exhibit a deviation from linearity, with the deviation tending to increase with increasing amount of dissolved AlSiMag 614. This is evident from the least squares fit to the Arrhenius equation given in Table 4. The coefficients of determination ( $r^2$ ) and standard deviations are not good, but even more discouraging is the fact that there is no uniform trend in either the pre-exponential or the activation energy with increasing alumina content.

As discussed in Section IIC, there are no good theoretical models which predict the observed temperature dependence of the viscosity of glass over any appreciable temperature range. This situation leads to the widespread use of empirical expressions with the most common being the Fulcher equation (Eq. 5), which has been repeatedly shown to represent the viscosity

\* 3M Company, St. Paul, Minn.

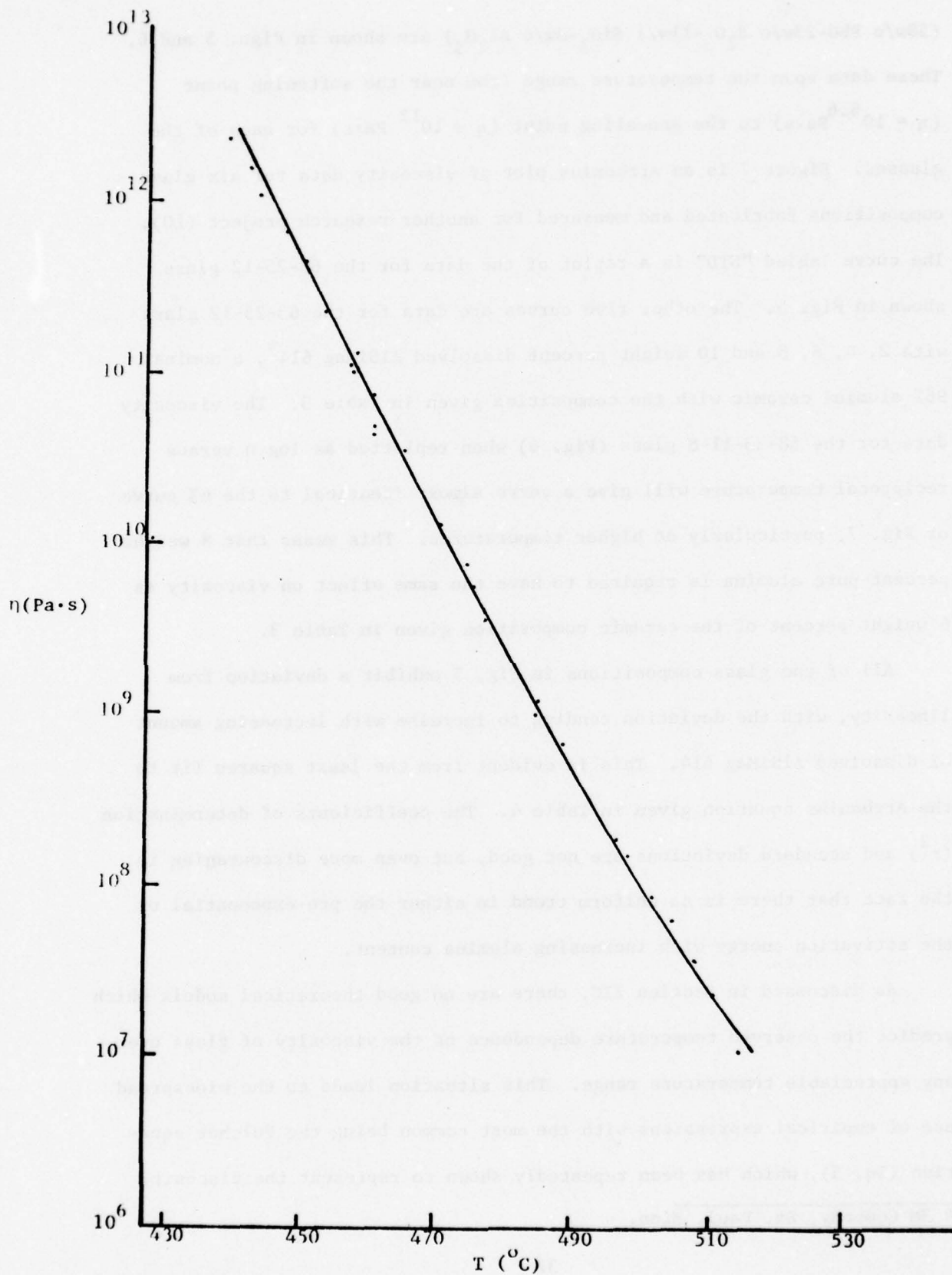


Figure 5. Viscosity of 63-25-12 Glass.

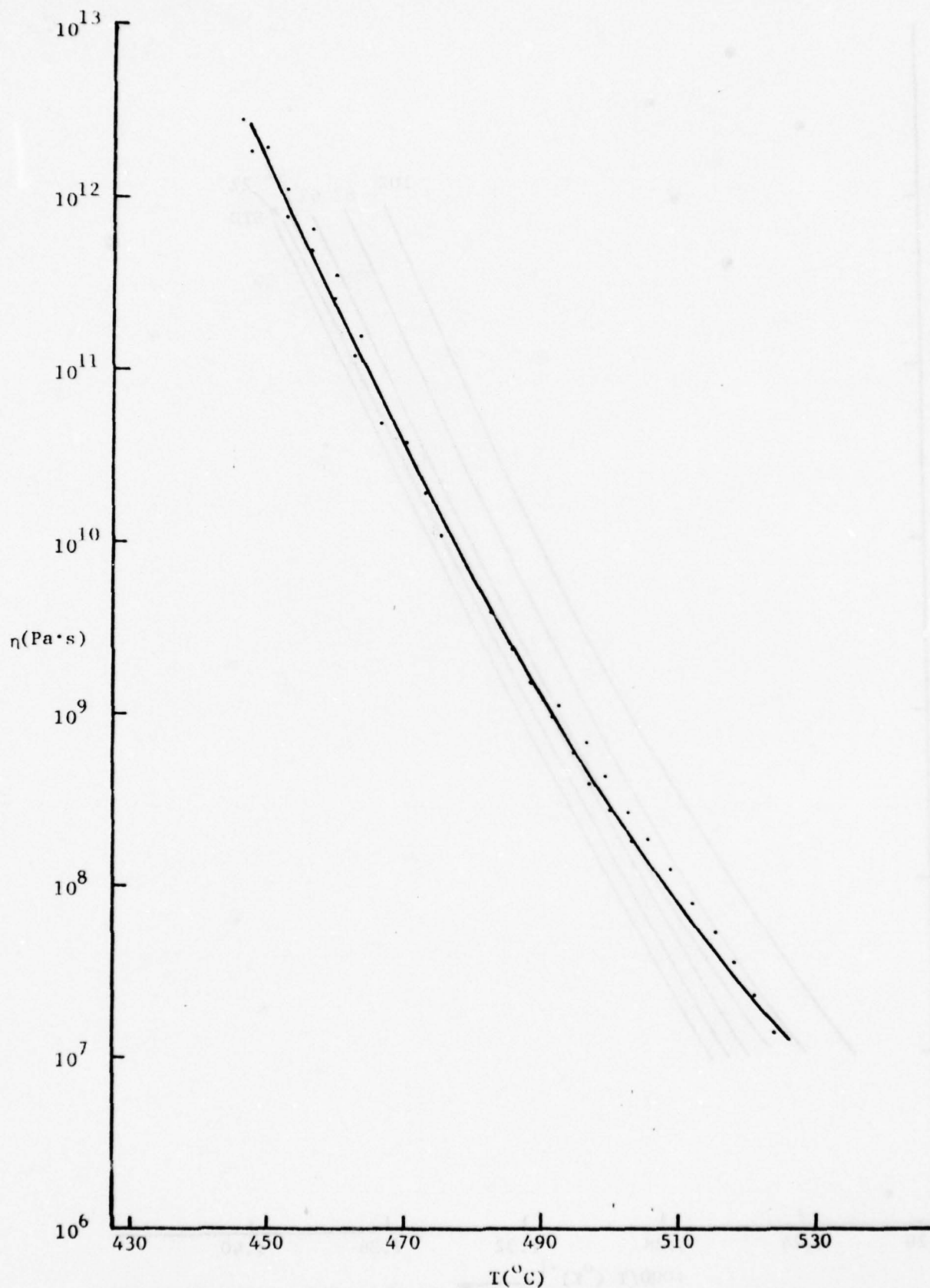


Figure 6. Viscosity of 58-23-11-8 Glass.



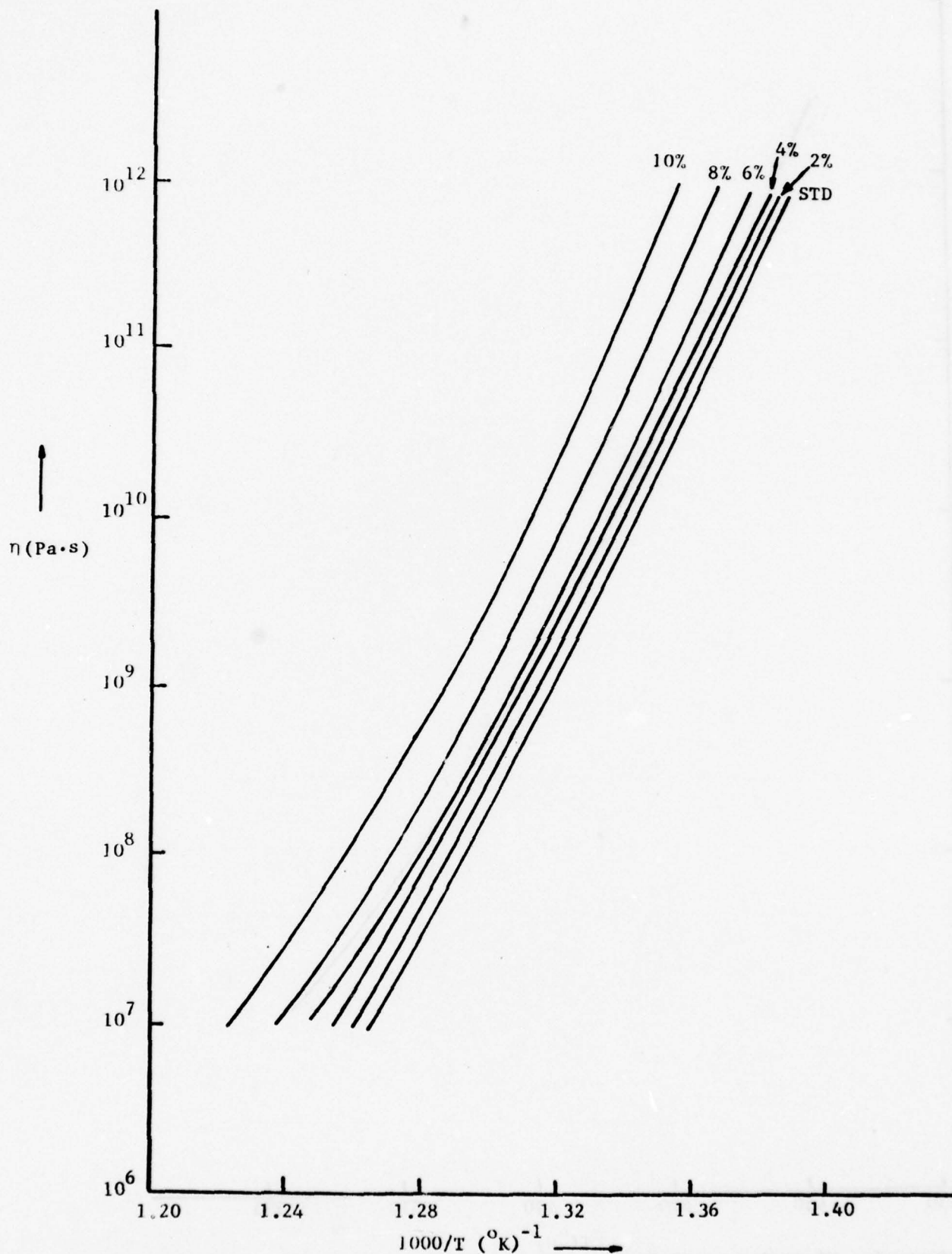


Figure 7. Viscosity of 63-25-12 Glass with Varying Weight Percents of Dissolved AlSiMag 614.

TABLE 3

## COMPOSITION OF AlSiMag 614 CERAMIC

Constituent	Weight Percent	
	Typical <sup>(1)</sup>	Analyzed <sup>(2)</sup>
Al <sub>2</sub> O <sub>3</sub>	96.0	94.7
SiO <sub>2</sub>	2.8	3.6
MgO	0.82	1.31
CaO	0.17	0.1
Fe <sub>2</sub> O <sub>3</sub>	0.09	0.2
Na <sub>2</sub> O	0.06	0.001
K <sub>2</sub> O	0.03	0.008
TiO <sub>2</sub>	0.03	0.02
BaO	--	0.008
Cr <sub>2</sub> O <sub>3</sub>	--	0.003
Ga <sub>2</sub> O <sub>3</sub>	--	0.03
Mn <sub>2</sub> O <sub>3</sub>	--	0.001
ZrO <sub>2</sub>	--	0.003

- (1) A typical analysis according to the manufacturer, 3M Company of St. Paul, Minnesota.
- (2) Bulk chemical analyses of the same lot of ceramic at RCA Laboratories, Princeton, New Jersey.

TABLE 4

ARRHENIUS EQUATION FIT FOR THE VISCOSITY OF EXPERIMENTAL  
GLASSES OVER FULL TEMPERATURE RANGE

$$\log \eta = a + b/T \quad (\eta \text{ in Pa}\cdot\text{s and } T \text{ in K})$$

Glass Composition	$r^2$	$\sigma$	a	b
Std. (63w/o PbO -25w/o B <sub>2</sub> O <sub>3</sub> -12w/o SiO <sub>2</sub> )	.9971	.0879	-44.1839 $\pm$ .4378	40389.5 $\pm$ 328.5
Std. + 2w/o AlSiMag 614	.9936	.1286	-42.4144 $\pm$ .7184	39179.1 $\pm$ 538.9
Std. + 4w/o AlSiMag 614	.9948	.1147	-40.7608 $\pm$ .6425	37988.1 $\pm$ 487.2
Std. + 6w/o AlSiMag 614	.9853	.1748	-42.8146 $\pm$ .9417	39674.7 $\pm$ 714.5
Std. + 8w/o AlSiMag 614	.9906	.1456	-42.8660 $\pm$ .7900	40002.4 $\pm$ 600.1
Std. + 10w/o AlSiMag 614	.9847	.1566	-39.8817 $\pm$ .9414	38013.7 $\pm$ 722.0
Std. + 8w/o Al <sub>2</sub> O <sub>3</sub>	.9931	.1332	-41.8464 $\pm$ .6981	38942.4 $\pm$ 525.6

of many glass compositions over rather wide temperature and viscosity ranges.

In order to apply linear regression analysis, Eq. 5 was rewritten as

$$T \log \eta = (B - AT_0) + AT + T_0 \log \eta \quad (11)$$

The coefficients  $(B - AT_0)$ ,  $A$ , and  $T_0$  were calculated, and the standard deviation of the data about the Fulcher curve,  $\sigma$ , determined from

$$\sigma^2 = (N - 3)^{-1} \sum_{i=1}^N [(\log \eta_i)_{\text{exp.}} - (\log \eta_i)_{\text{calc.}}]^2 \quad (12)$$

where  $N$  is the number of data points and the summation is over the square of the differences between experimental and calculated values of log viscosity. The results of these calculations are given in Table 5, and the statistical fit to the experimental data is seen to be excellent; the coefficients of determination ( $r^2$ ) are all 0.999 or greater and the standard deviations, calculated from Eq. 12, are considerably less than the anticipated experimental scatter of the viscosity data. Even though the fit is excellent, the fact that  $A$ ,  $B$  and  $T_0$  are purely empirical parameters with no physical significance is amply demonstrated by two observations based on the data in Table 5: (1) none of the three parameters show any correlation with increasing amount of dissolved alumina; and (2) the values of  $A$ ,  $B$  and  $T_0$  are considerably different for the 6% substrate glass and the 8% alumina glass even though the curves of  $\log \eta$  versus either  $T$  or  $1/T$  are almost indistinguishable for these two glass compositions.

There is more basis in theory to use the two parameter Arrhenius equation (Eq. 6) to represent the viscosity providing the temperature range is sufficiently small. The fact that none of the glass compositions give a straight line on Fig. 7 means that the activation energy, or the pre-



TABLE 5

## FULCHER EQUATION FIT FOR EXPERIMENTAL GLASSES

$$\text{Log } \eta = A + B/(T-T_0) \quad (\eta \text{ in Pa}\cdot\text{s and } T \text{ in K})$$

Glass Composition	$r^2$	$\sigma$	A	B	$T_0$
Std. (63w/o Pbo -25w/o B <sub>2</sub> O <sub>3</sub> -12w/o SiO <sub>2</sub> )	.9988	.0576	-2.11486	1916.50	585.02
Std. + 2w/o AlSiMag 614	.9994	.0389	-1.59694	1793.72	590.56
Std. + 4w/o AlSiMag 614	.9992	.0456	-4.19376	2794.29	549.85
Std. + 6w/o AlSiMag 614	.9995	.0323	-0.07368	1284.22	621.95
Std. + 8w/o AlSiMag 614	.9996	.0313	-0.42431	1475.82	612.77
Std. + 10w/o AlSiMag 614	.9997	.0225	1.60434	947.40	647.25
Std. + 8w/o Al <sub>2</sub> O <sub>3</sub>	.9994	.0387	-1.07364	1695.24	595.53

exponential term, or both change with temperature over the range of the experiments. The temperature dependence of the activation energy,  $Q$ , and the pre-exponential term,  $A$ , were investigated for each of the glass compositions by calculating  $\eta$  at two closely temperatures from the Fulcher equation fit and using these data points to calculate  $Q$  and  $A$ ; the results of those calculations are shown in Figs. 8 and 9. Both  $Q$  and  $\log A$  for each of the glass compositions are seen to decrease with increasing temperature and approach values ( $Q = 339$  kJ/mol and  $\log A = 14.3$  determined in an earlier study (7) for the standard glass over the temperature range  $650-800^{\circ}\text{C}$ . An activation energy that is constant at high temperatures and increases with decreasing temperature has also been observed for other glass systems (21), but no satisfactory theoretical explanation of this phenomenon has been advanced. The divergence of the  $Q$  and  $\log A$  values for the different glass compositions at low temperatures is felt to reflect scatter in the experimental data rather than any systematic composition dependent effect.

It is apparent from an examination of Figs. 8 and 9 that the Arrhenius equation will not provide an adequate fit to the experimental data over the full temperature span of the measurements, even though the total temperature change is less than  $100^{\circ}\text{C}$ . Following the ideas discussed in Section IIC, a critical point was arbitrarily selected at  $\log \eta = 9$  and data for each of the various glass compositions fit to an Arrhenius equation for temperatures both above and below this point; the results of these calculations are given in Table 6. The statistical parameters indicate a rather poor fit in both regions, but the results are encouraging in two respects: (1) the  $a$  and  $b$  parameters in the high temperature region ( $\log \eta < 9.0$ ) show a monotonic change with increasing alumina content; and (2) the  $a$  and

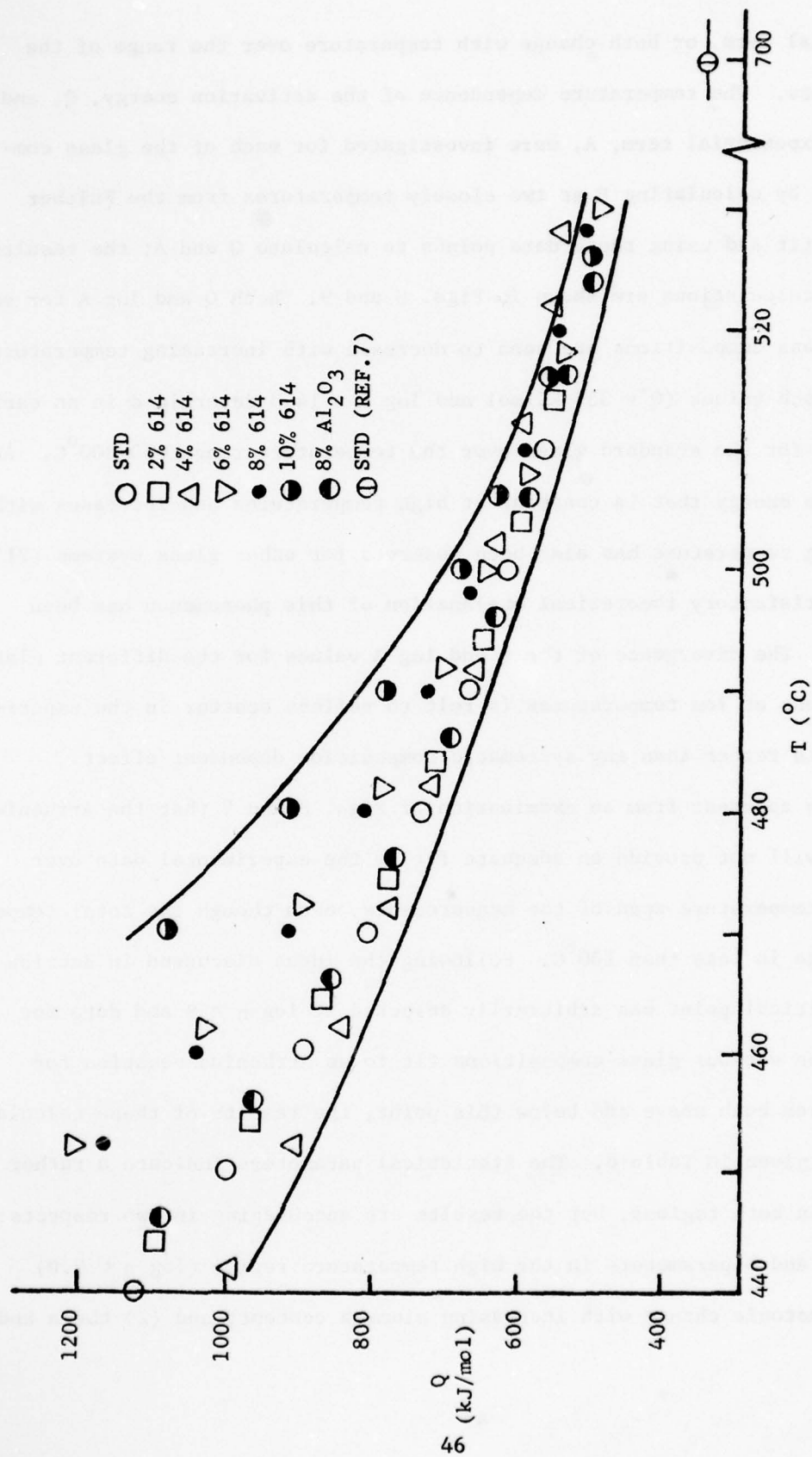


Figure 8. Temperature Dependence of the Activation Energy for an Arrhenius Equation Fit to the Viscosity.

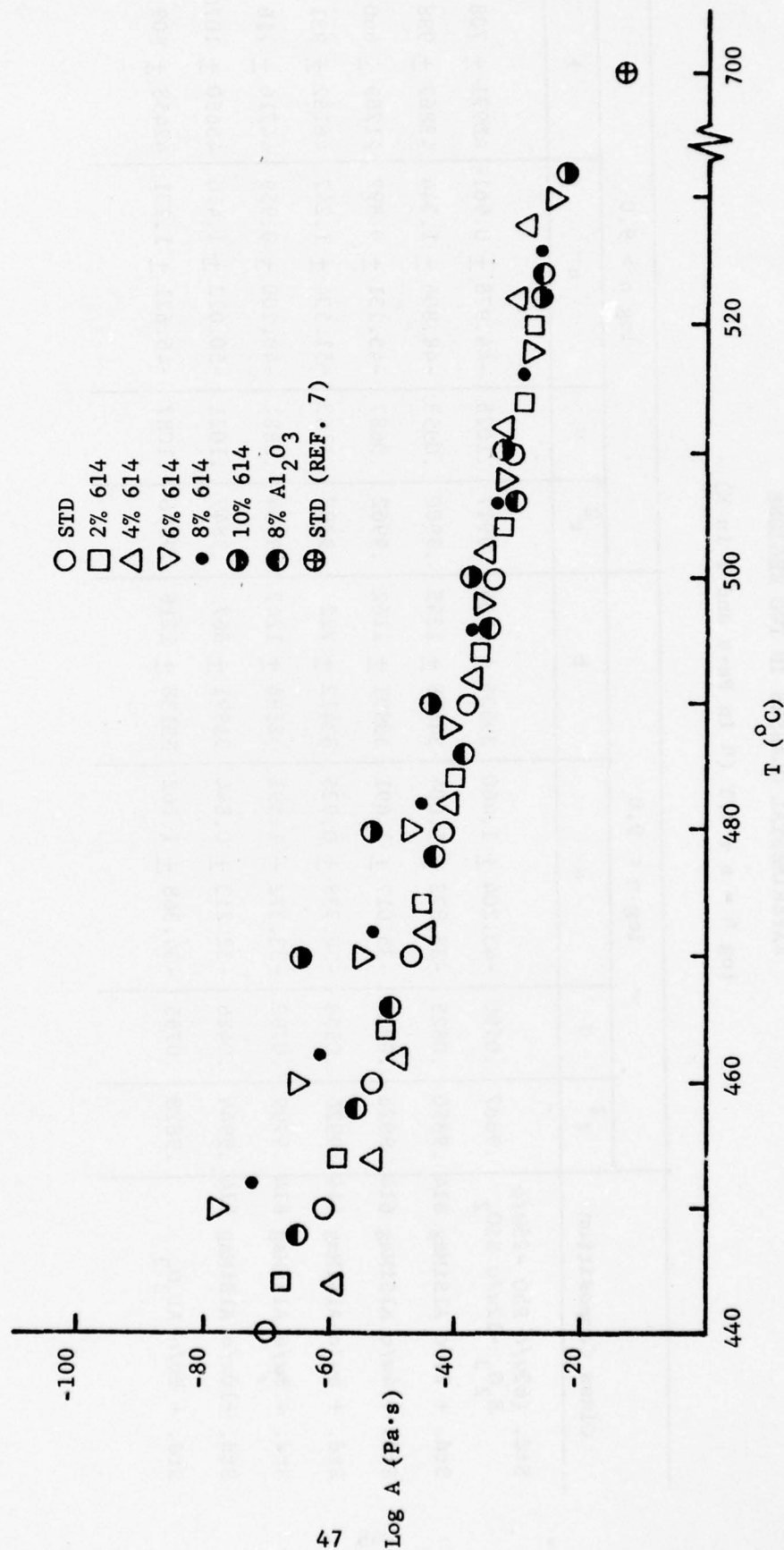


Figure 9. Temperature Dependence of Pre-exponential Term for an Arrhenius Equation  
Fit to the Viscosity.



TABLE 6

ARRHENIUS EQUATION FIT FOR THE VISCOSITY OF  
EXPERIMENTAL GLASSES IN TWO REGIONS

$$\log \eta = a + b/T \quad (\eta \text{ in Pa}\cdot\text{s and } T \text{ in K})$$

Glass Composition	$\log \eta < 9.0$				$\log \eta > 9.0$			
	$r^2$	$\sigma$	a	b	$r^2$	$\sigma$	a	b
Std. (63w/o PbO -25w/o B <sub>2</sub> O <sub>3</sub> -12w/o SiO <sub>2</sub> )	.9887	.0500	-43.204 $\pm$ 1.460	39636 $\pm$ 1134	.9917	.1025	-44.978 $\pm$ 0.961	40971 $\pm$ 708
Std. + 2w/o AlSiMag 614	.9850	.0825	-36.872 $\pm$ 1.604	34898 $\pm$ 1245	.9900	.0953	-48.806 $\pm$ 1.344	43867 $\pm$ 988
Std. + 4w/o AlSiMag 614	.9828	.0924	-35.617 $\pm$ 1.491	33991 $\pm$ 1162	.9962	.0687	-45.231 $\pm$ 0.892	41289 $\pm$ 660
Std. + 6w/o AlSiMag 614	.9926	.0596	-34.738 $\pm$ 0.925	33412 $\pm$ 722	.9887	.1143	-51.534 $\pm$ 1.247	46162 $\pm$ 931
Std. + 8w/o AlSiMag 614	.9799	.0792	-33.372 $\pm$ 1.591	32596 $\pm$ 1247	.9934	.0881	-49.200 $\pm$ 0.959	44716 $\pm$ 716
Std. +10w/o AlSiMag 614	.9944	.0426	-32.213 $\pm$ 0.844	31991 $\pm$ 667	.9849	.1021	-50.022 $\pm$ 1.416	45660 $\pm$ 1070
Std. + 8w/o Al <sub>2</sub> O <sub>3</sub>	.9828	.0765	-34.368 $\pm$ 1.562	33138 $\pm$ 1216	.9896	.1087	-46.621 $\pm$ 1.231	42458 $\pm$ 909

b parameters of the glass with 8w/o  $\text{Al}_2\text{O}_3$  are the same, within one  $\sigma$ , as those of the glass with 6w/o AlSiMag 614 in the high temperature region. Thus, it appears that the temperature dependence of the viscosity of all of the glass compositions exhibits Arrhenius behavior at sufficiently high temperatures, certainly, for all temperatures above the softening point. At temperatures below the softening point we were unable to correlate the data with any model having physical significance.

### C. Sintering

#### 1. Apparatus and Procedure

Neck growth measurements between spherical glass particles were conducted utilizing a modified hot stage metallograph with the regular camera system removed and replaced by a video camera. A second video camera was used to monitor a digital clock and a digital volt meter that measured the sample thermocouple emf. A special effects generator was used to combine the two video signals so that the time and the thermocouple emf were positioned at the bottom of the image on the TV monitor screen. All information thus obtained was recorded on a video recorder with stop-frame capability. The atmosphere in the hot stage was dry air produced by passing compressed air over anhydrous calcium sulfate before entering the hot stage. The flow rate was sufficiently low (15 ml/min) that equilibrium partial pressure of water vapor ( $\sim 0.66$  Pa) could be assumed. The experimental procedure consisted of placing a few glass spheres of similar size in a platinum pan on the hot stage unit and locating two particles touching each other so that the radius of the neck that grows between them could be measured as a function of time at constant temperature. The furnace

in the hot stage was heated to the required temperature and the neck growth, time, and thermocouple emf were recorded continuously on video tape during the sintering process. This method of recording data was useful because it created a virtually continuous and complete record of the sintering process and all data for a particular temperature could be taken on the same pair of glass spheres.

For initial stage sintering of two spherical particles, the particle radius,  $r$ , and the neck radius,  $x$ , are the important geometric parameters. If the material in the neck region behaves as a Newtonian viscous fluid, the relative neck growth,  $x/r$ , should be related to time,  $t$ , according to the following relationship derived by Frenkel (42).

$$\left(\frac{x}{r}\right)^2 = \frac{3}{2} \frac{\gamma}{\eta} r^{-1} t \quad (13)$$

In Eq. 13,  $\eta$  is the viscosity of the material undergoing sintering and  $\gamma$  is its surface tension.

## 2. Results and Discussion

The relative neck growth data for the standard glass and standard glass with 8% alumina are shown in Figs. 10 and 11, and the linear dependence of  $(x/r)^2$  with time predicted by Eq. 13 is seen to hold quite well. The surface tension to viscosity ratios were calculated according to Eq. 13 at each of the measurement temperatures for the two glass compositions, and the results of these calculations are shown in Fig. 12.

It was originally hoped that the magnitude and temperature dependence of the surface tension could be determined by combining the sintering and viscosity data. This approach did not prove to be fruitful due to the

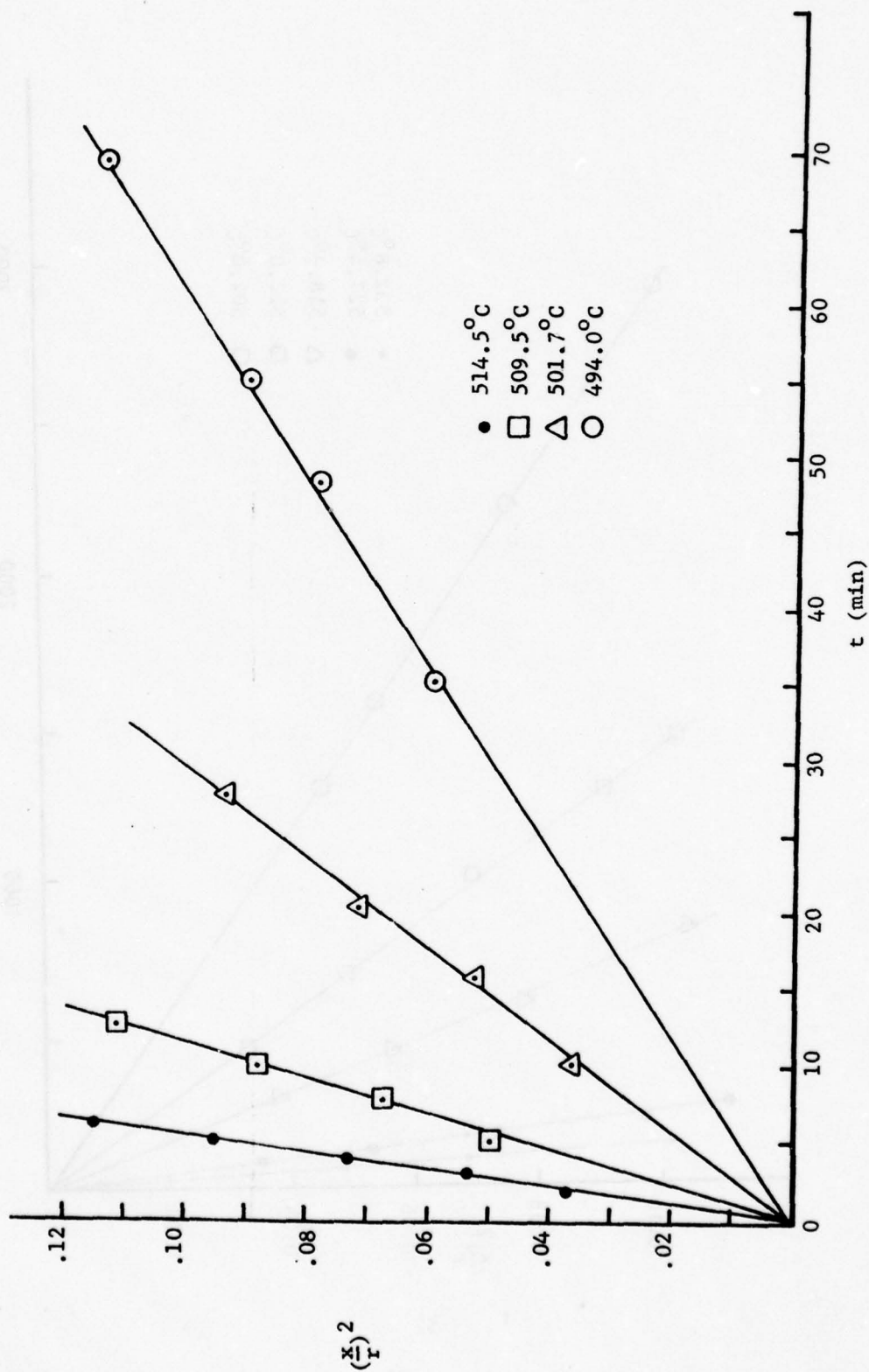


Figure 10. Initial Stage Sintering Kinetics for 63-25-12 Glass in Dry Air.



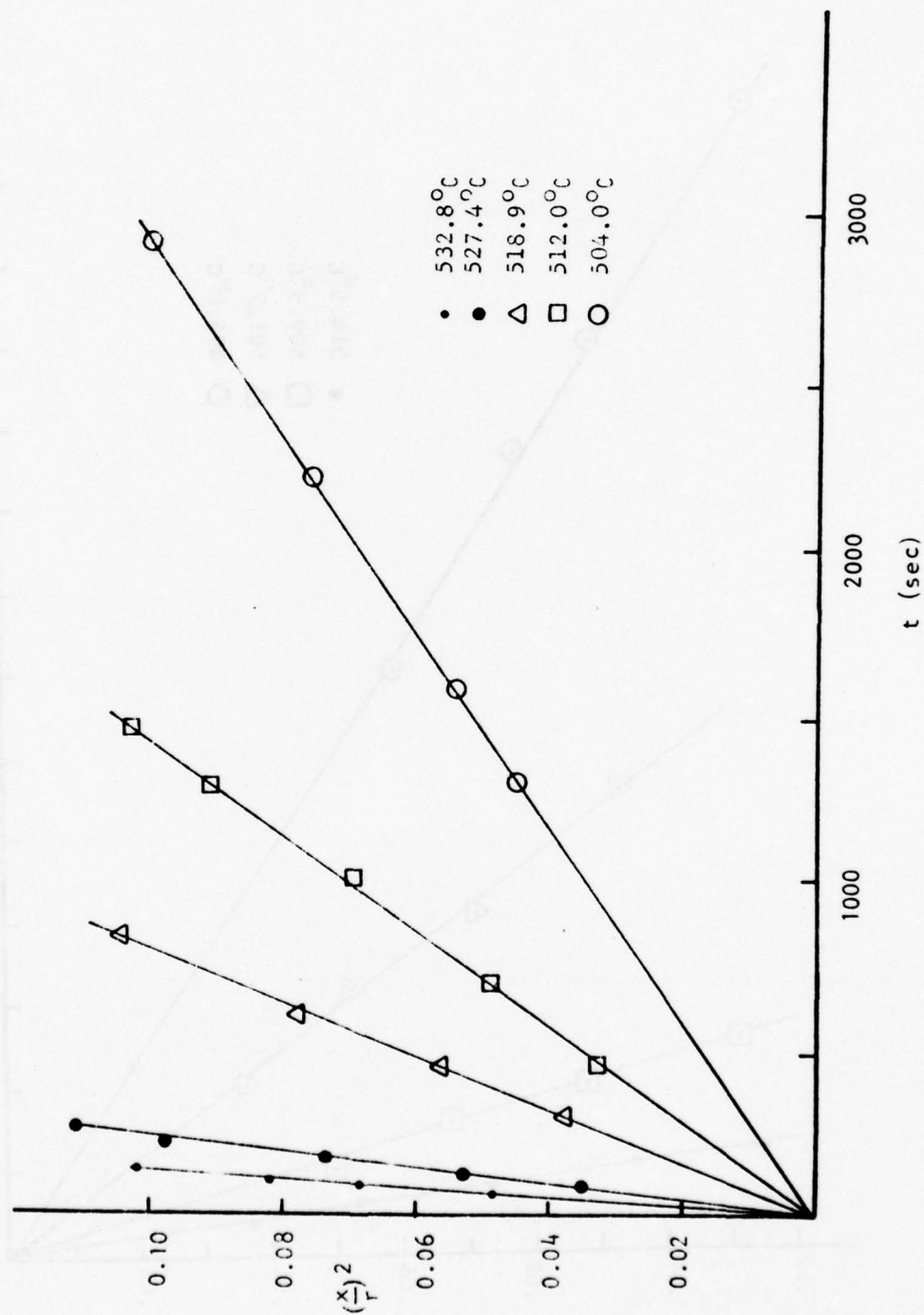


Figure 11. Initial Stage Sintering Kinetics for 58-23-11-8 Glass in Dry Air.

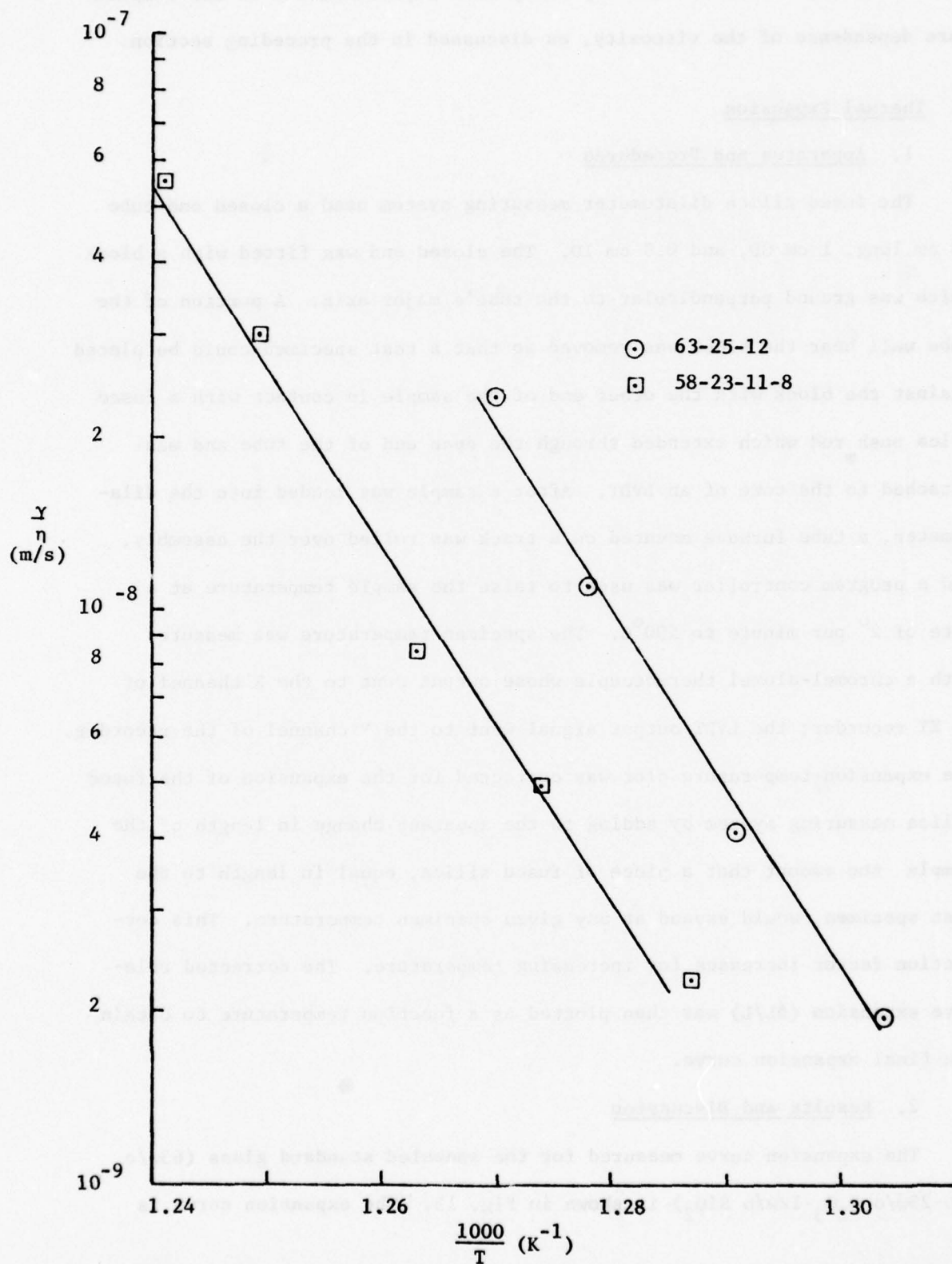


Figure 12. Effect of 8w/o Dissolved Alumina on the Surface Tension to Viscosity Ratio of Standard Glass.

uncertainties associated with any analytical representation of the temperature dependence of the viscosity, as discussed in the preceding section.

#### D. Thermal Expansion

##### 1. Apparatus and Procedures

The fused silica dilatometer measuring system used a closed end tube 33 cm long, 1 cm OD, and 0.8 cm ID. The closed end was fitted with a block which was ground perpendicular to the tube's major axis. A portion of the tube wall near the block was removed so that a test specimen could be placed against the block with the other end of the sample in contact with a fused silica push rod which extended through the open end of the tube and was attached to the core of an LVDT. After a sample was loaded into the dilatometer, a tube furnace mounted on a track was rolled over the assembly, and a program controller was used to raise the sample temperature at a rate of  $2^{\circ}$  per minute to  $500^{\circ}\text{C}$ . The specimen temperature was measured with a chromel-alumel thermocouple whose output went to the X channel of an XY recorder; the LVDT output signal went to the Y channel of the recorder. The expansion-temperature plot was corrected for the expansion of the fused silica measuring system by adding to the apparent change in length of the sample the amount that a piece of fused silica, equal in length to the test specimen, would expand at any given specimen temperature. This correction factor increases for increasing temperature. The corrected relative expansion ( $\Delta L/L$ ) was then plotted as a function temperature to obtain the final expansion curve.

##### 2. Results and Discussion

The expansion curve measured for the annealed standard glass (63w/o  $\text{PbO}$ -25w/o  $\text{B}_2\text{O}_3$ -12w/o  $\text{SiO}_2$ ) is shown in Fig. 13. The expansion curve is

not a straight line, and so the mean linear expansion coefficient, defined by Eq. 4, is not a constant but increases with increasing temperature. The values of  $\bar{\alpha}$  obtained from Fig. 13 for four different temperature ranges are given in Table 7. It is seen that  $\bar{\alpha}$  increases by almost 30% as the upper temperature is increased from 100 to 400°C. The most common temperature range quoted in the literature for linear thermal expansion of glasses is room temperature to 300°C, and the variations shown in Table 7 underscore the necessity of knowing the temperature range of the measurements.

Thermal expansion measurements were also carried out for glass compositions made by dissolving 4 and 8 weight percent  $\text{Al}_2\text{O}_3$  in the standard glass. The mean linear expansion coefficients from room temperature to 300°C calculated from these measurements are given in Table 8. The addition of alumina to the lead borosilicate glass tends to lower the linear expansion coefficient, in agreement with Reference A1. Also shown in Table 8 are the coefficients predicted using the principle of additivity applied to compositions in the  $\text{PbO} \cdot 2\text{B}_2\text{O}_3$  primary phase field as discussed in Section IIB. The equation used was

$$\begin{aligned} \bar{\alpha} = & 1.162(\text{m/o PbO}) + 0.476(\text{m/o B}_2\text{O}_3) + 0.387(\text{m/o SiO}_2) \\ & + 0.447(\text{m/o Al}_2\text{O}_3) \end{aligned} \quad (14)$$

Thermal expansion curves were run on unannealed samples of the standard glass and the standard glass with 8% alumina as shown in Figs. 14 and 15. There are two primary differences in the expansion curves for the unannealed versus the annealed glasses: (1) the 23-300°C coefficients are smaller for the unannealed samples, 61 versus 71 for the unannealed and annealed standard glass and 57 versus 64 for the unannealed and annealed 8% alumina glass; and



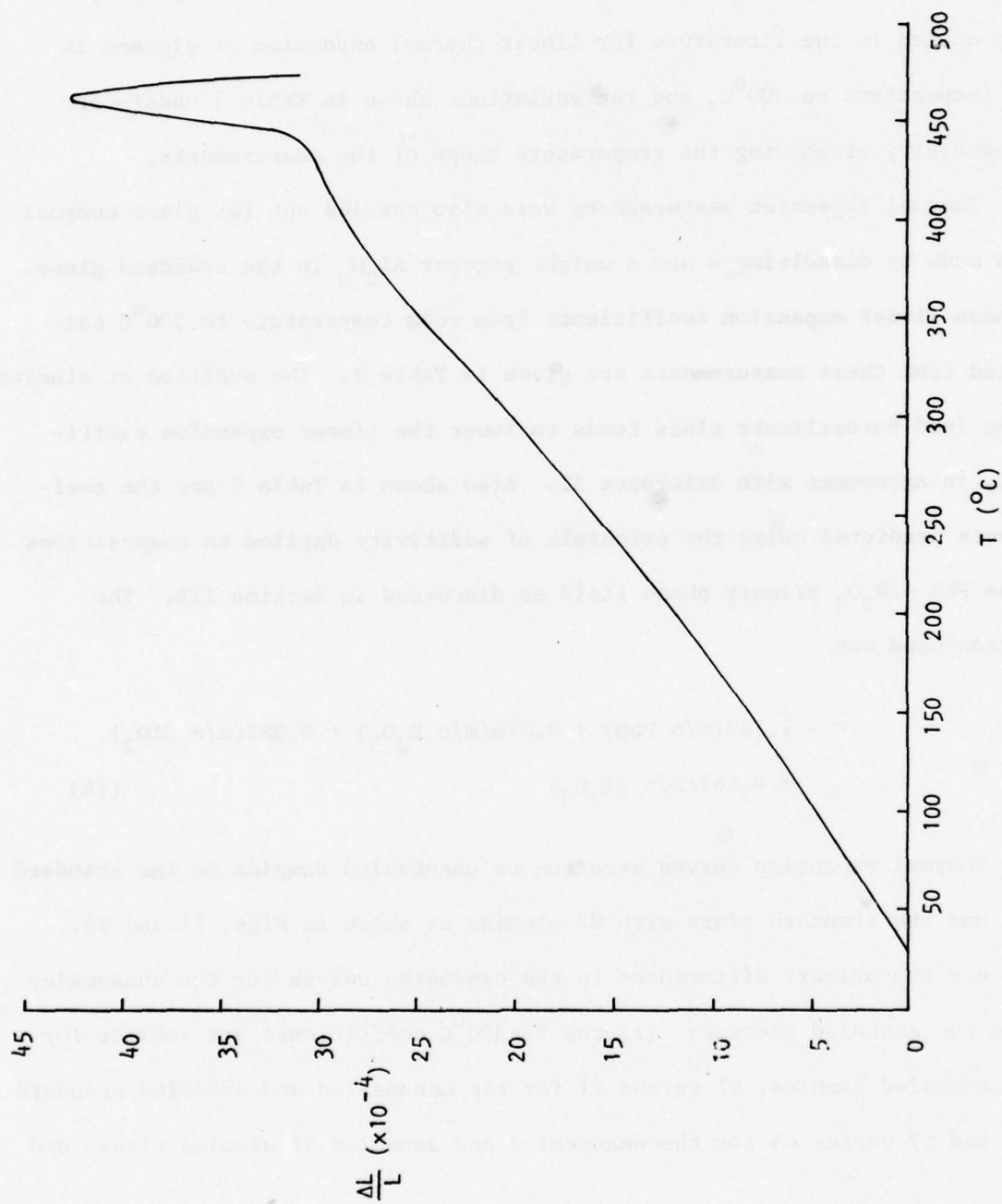


Figure 13. Thermal Expansion of Annealed 63-25-12 Glass.

TABLE 7

MEAN COEFFICIENT OF LINEAR EXPANSION FOR  
63-25-12 GLASS FOR DIFFERENT TEMPERATURE RANGES

Temp. Range ( $^{\circ}\text{C}$ )	$\bar{\alpha}$ ( $10^{-7}/^{\circ}\text{C}$ )
23-100	58
23-200	65
23-300	71
23-400	75

TABLE 8

MEAN COEFFICIENTS OF LINEAR EXPANSION  
FOR EXPERIMENTAL GLASSES

Glass Composition	$\bar{\alpha}$ (R.T.-300 $^{\circ}\text{C}$ ) ( $10^{-7}/^{\circ}\text{C}$ )	
	Measured	Calculated
63w/oPbO-25w/oB <sub>2</sub> O <sub>3</sub> -12w/oSiO <sub>2</sub>	71	68.5
60.5w/oPbO-24w/oB <sub>2</sub> O <sub>3</sub> -11.5w/oSiO <sub>2</sub> -4w/oAl <sub>2</sub> O <sub>3</sub>	68	67.4
58w/oPbO-23w/oB <sub>2</sub> O <sub>3</sub> -11w/oSiO <sub>2</sub> -8w/oAl <sub>2</sub> O <sub>3</sub>	64	66.4

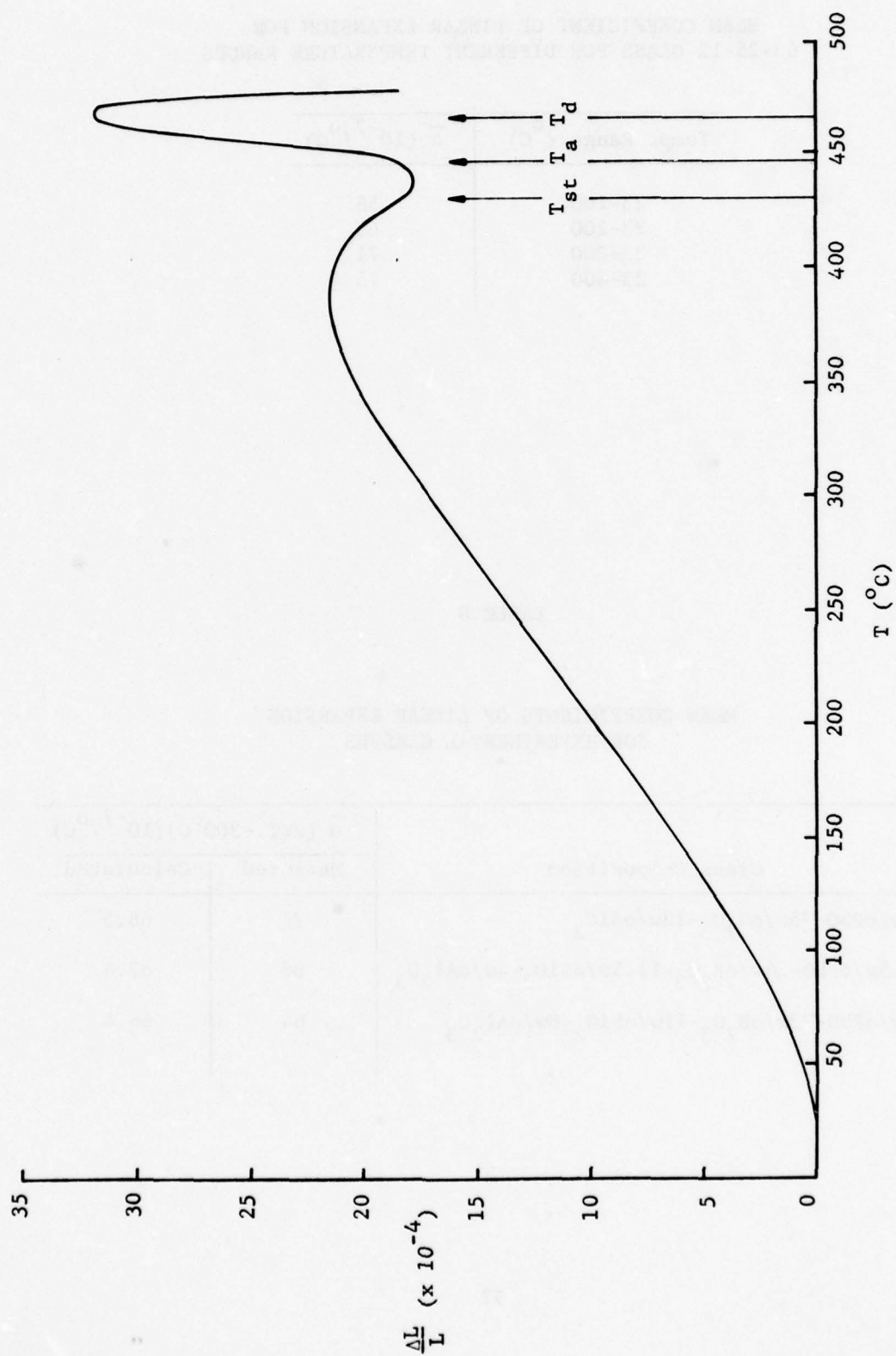


Figure 14. Thermal Expansion of Unannealed 63-25-12 Glass.

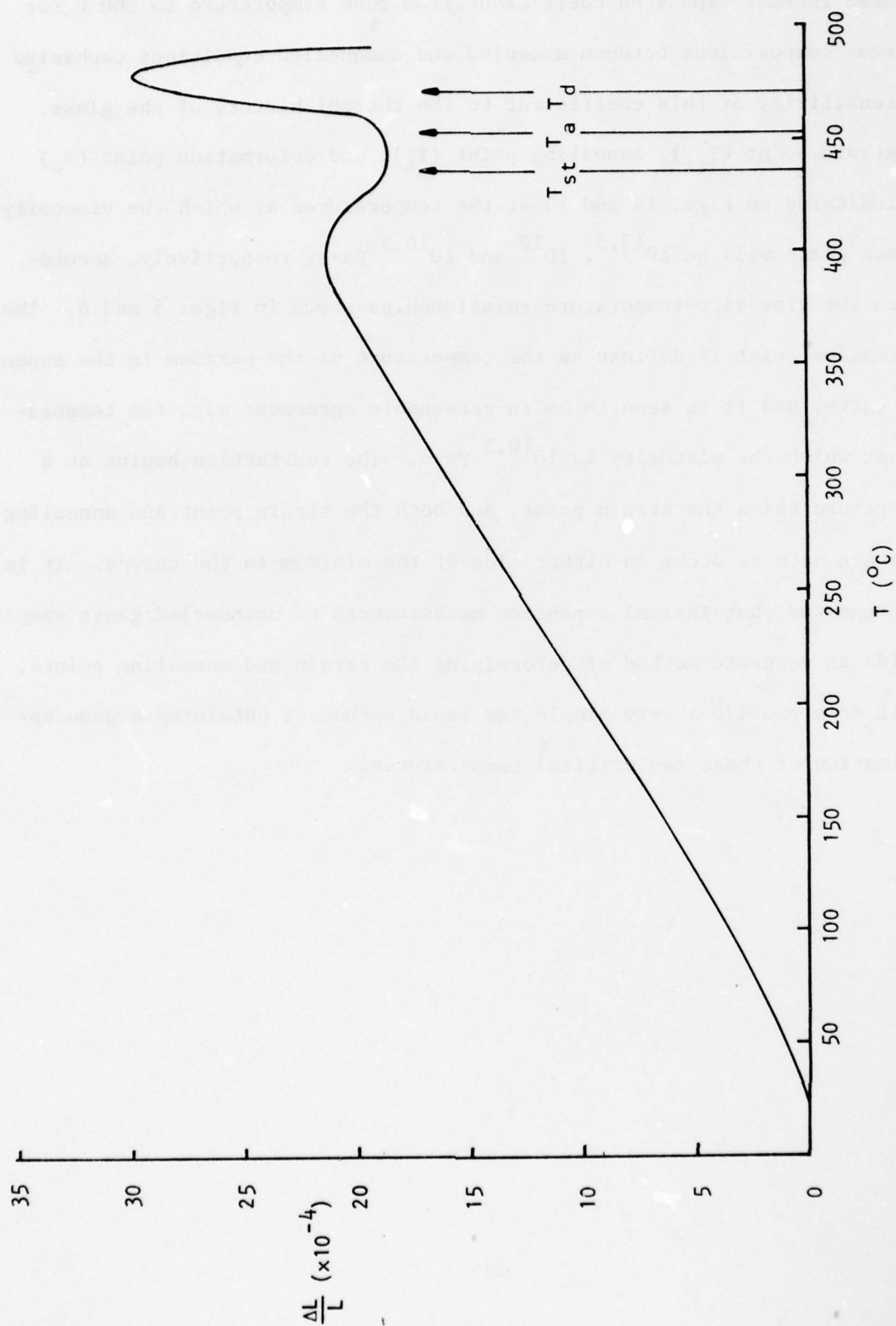


Figure 15. Thermal Expansion of Unannealed 58-23-11-8 Glass.



(2) the unannealed samples show a significant contraction prior to the rapid expansion to the deformation point. The variations of 12 and 16% in the mean thermal expansion coefficient from room temperature to 300°C for the same compositions between annealed and unannealed conditions emphasize the sensitivity of this coefficient to the thermal history of the glass. The strain point ( $T_{st}$ ), annealing point ( $T_a$ ), and deformation point ( $T_d$ ) are indicated on Figs. 14 and 15 at the temperatures at which the viscosity of each glass will be  $10^{13.5}$ ,  $10^{12}$  and  $10^{10.5}$  Pa·s, respectively, according to the viscosity-temperature relationships shown in Figs. 5 and 6. The deformation point is defined as the temperature of the maximum in the expansion curve, and it is seen to be in reasonable agreement with the temperature at which the viscosity is  $10^{10.5}$  Pa·s. The contraction begins at a temperature below the strain point, and both the strain point and annealing point are seen to occur on either side of the minimum in the curves. It is not suggested that thermal expansion measurements on unannealed glass samples provide an accurate method of determining the strain and annealing points, but it does provide a very simple and rapid method of obtaining a good approximation of these two critical temperatures.

#### IV. SUMMARY

The first major conclusion that can be drawn based on the review of the literature and the experimental studies conducted during this project is that quantitative correlations between physical properties and chemical composition of glasses are only possible over very limited composition ranges at constant temperature. While some success was demonstrated in applying the principle of additivity (e.g., the mean coefficient of linear expansion for glass compositions in the  $\text{PbO} \cdot 2\text{B}_2\text{O}_3$  primary phase field of the  $\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  system, and the surface tension of glass compositions in the  $3\text{BaO} \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$  primary phase field of the  $\text{BaO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  system) the quantity of data required in a small composition range is such that the general usefulness is limited. The primary reason for the failure of property-composition relationships to hold over wider composition ranges is that glasses are not homogeneous materials. There is widespread evidence of surface segregation, metastable immiscibility, and phase separation in glass systems, and the extent of these effects can be more important in influencing physical properties than the overall composition.

The second major conclusion that can be drawn is that present theoretical models which describe the temperature dependence of the thermal expansion, surface tension, or viscosity of glasses are woefully inadequate. One of the major reasons for this failure is, again, the fact that glasses are not homogeneous materials. Until advanced theoretical models are developed incorporating the microstructure of the glass, the only recourse in order to interpolate or extrapolate experimental measurements is to use empirical equations, such as the Fulcher equation for viscosity, which

contain a sufficient number of constants to adequately represent each set of experimental data over the temperature range of the experiments. The collection of physical property data on low alkali glasses of known composition presented in this report is the most complete yet published. The data compilations presented in Appendixes A-D should have particular usefulness to scientists and engineers concerned with the development and application of electronic glasses, and should be of general interest to the glass industry as a whole.

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## APPENDIX A

### Thermal Expansion Data

#### Explanation of Column Headings for Tables A1-A5

##### 1. Composition

For most of the glass compositions the concentrations of all constituent oxides are given in both mole percent (m/o) and weight percent (w/o). For a few of the multi-component glasses, the concentrations of the major constituents are given in weight percent only, and the minor constituents' concentrations are given in the "Other" column as weight percent of the oxide of the element listed.

##### 2. $\bar{\alpha}$

The mean coefficients of linear thermal expansion in units of  $10^{-7}/^{\circ}\text{C}$  are given for the temperature span room temperature to  $300^{\circ}\text{C}$  unless otherwise indicated.

##### 3. $T_d$

The deformation temperature in  $^{\circ}\text{C}$  is listed whenever available for the glass composition.  $T_d$  is the temperature at which viscous flow counteracts expansion, and corresponds to a glass viscosity of  $10^{10}$  to  $10^{11}$  Pa·s.

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TABLE A1

## Lead Borosilicate Glasses

Glass No.	PbO		$B_2O_3$		$SiO_2$		$\bar{\alpha}$	$T_d$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o			
1	2.9	10.0	9.2	9.7	87.9	80.3	21.0	737	A1
2	2.7	8.9	28.0	29.1	69.3	62.0	34.0	624	A1
3	6.4	19.8	20.0	19.2	73.6	61.0	32.0	722	A1
4	10.3	29.5	11.1	9.9	78.6	60.6	31.0	b*	A1
5	6.4	19.4	30.4	28.9	63.2	51.7	37.0	655	A1
6	3.0	9.9	18.7	19.5	78.4	70.6	28.0	685	A1
7	6.3	19.8	10.3	10.0	83.4	70.2	25.0	735	A1
8	2.7	8.7	38.8	39.7	58.5	51.6	47.0	535	A1
9	8.5	24.8	26.3	24.0	65.2	51.2	40.0	696	A1
10	10.7	30.1	22.0	19.2	67.3	50.7	39.0	b	A1
11	15.4	39.9	12.4	10.0	72.1	50.1	42.0	b	A1
12	3.2	10.1	49.1	48.9	47.8	41.0	54.0	519	A1
13	6.7	20.0	42.8	39.7	50.4	40.3	48.0	546	A1
14	11.0	30.2	34.2	29.3	54.8	40.5	46.0	b	A1
15	16.0	40.4	25.1	19.7	58.9	39.9	47.0	b	A1
16	21.8	50.2	14.2	10.2	64.0	39.6	53.0	b	A1
17	16.2	40.2	37.7	29.1	64.1	30.7	54.0	b	A1
18	22.3	50.2	28.3	19.9	49.4	29.9	53.0	b	A1
19	29.6	60.1	16.3	10.3	54.2	29.6	79.0	487	A1
20	30.5	60.4	31.5	19.4	38.0	20.2	63.0	475	A1
21	39.6	69.9	18.5	10.2	41.9	19.9	79.0	460	A1
22	31.1	60.1	49.6	29.9	19.3	10.0	70.0	498	A1
23	41.0	70.1	37.3	19.9	21.7	10.0	76.0	461	A1
24	53.6	80.0	21.7	10.1	24.7	9.9	98.0	392	A1
25	22.4	51.0	14.1	10.0	63.6	39.0	45.2		A2
26	25.7	55.6	14.8	10.0	59.5	34.6	47.2		A2
27	29.4	59.9	16.1	10.2	54.6	29.9	55.3		A2
28	33.4	62.8	42.9	25.2	23.7	12.0	64.5		A2
29	40.8	70.9	18.6	10.1	40.6	19.0	72.3		A2
30	42.8	71.0	48.3	25.0	89.0	4.0	75.0		A2
31	47.3	75.8	20.1	10.2	32.5	14.0	84.0		A2
32	54.6	80.6	22.2	10.2	23.2	9.2	95.5		A2
33	33.5	63.0	42.7	25.0	23.8	12.0	71.0	465	This work

\* b Sample crystallized before normal deformation temperature.



TABLE A2

## Lead Borosilicate Glasses Plus Alumina

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		$\bar{\alpha}$	T <sub>d</sub>	Reference
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o			
34	51.5	75.0	24.2	11.0	7.7	3.0	16.5	11.0	84.0		A3a
35	58.9	82.0	23.0	10.0	13.4	5.0	4.7	3.0	104.0		A3b
36	2.9	9.4	18.1	18.6	75.9	67.2	3.2	4.8	24.0	703	Al
37	6.1	18.8	9.9	9.5	80.6	66.9	3.4	4.8	23.0	719	Al
38	2.6	8.3	37.6	37.8	56.6	49.1	3.3	4.8	46.0	561	Al
39	8.2	23.6	25.6	22.9	62.8	48.8	3.6	4.8	38.0	658	Al
40	14.8	38.0	11.9	9.5	69.2	47.7	4.1	4.8	37.0	596	Al
41	6.5	19.0	40.7	36.9	49.1	38.4	3.6	4.8	44.0	576	Al
42	10.6	28.8	32.9	27.9	52.7	38.6	3.9	4.8	43.0	645	Al
43	15.3	38.4	24.1	18.8	56.4	38.0	4.2	4.8	44.0	643	Al
44	28.0	57.2	15.4	9.8	51.4	28.2	5.2	4.8	59.0	514	Al
45	29.4	57.2	47.0	28.5	18.2	9.5	5.4	4.8	66.0	496	Al
46	50.0	76.2	20.2	9.6	22.9	9.4	6.9	4.8	93.0	409	Al
47	35.5	65.5	15.5	8.9	45.2	22.4	3.8	3.2	60.0	449	A4a
48	32.0	60.5	40.7	24.0	22.6	11.5	4.6	4.0	68.0	468	This work
49	30.5	58.0	38.8	23.0	21.5	11.0	9.2	8.0	64.0	472	This work

TABLE A3

## Other Lead Containing Glasses

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		ZnO		TiO <sub>2</sub>		Other	$\bar{\alpha}$	T <sub>d</sub>	Reference
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o				
50			28.7	60.0	71.3	40.0					3.1Al, 3.1Cd, 1Zr, 1.5Na	56.7*		A5
51			38.5	70.0	61.5	30.0					3.5Al, 2.6Cd, 0.5Zr	73.8*		A5
52		51		8.8		30			2			60.0*	485	A4b
53		52.5		10		31						52.0*	495.5	A4c
54	63.1	82.3	21.8	8.8	0.3	1.0	14.6	6.9	0.22	1.0	Bi <sub>2</sub> O <sub>3</sub> -1.2m/o (3.15w/o)	105.0	330	A6
55	63.1	80.2	21.8	8.6	0.3	1.0	13.4	6.1	0.22	1.0	CuO-4.0m/o (1.8w/o)	122.0	324	A6
56	63.1	80.2	21.8	8.6	0.3	1.0	14.6	4.3	0.22	1.0	Bi <sub>2</sub> O <sub>3</sub> -1.2m/o (3.14w/o)	124.0	314	A6
57	63.1	71.8	21.8	8.8	0.3	1.0	13.4	6.8	0.22	1.0	PbF <sub>2</sub> -7.5m/o (10.7w/o)	131.0	299	A6
58	63.6	84.0	21.8	9.0			14.6	7.1			Bi <sub>2</sub> O <sub>3</sub> -1.2m/o (3.15w/o)			A6
59	63.6	83.8	21.8	9.0			5.6	2.7			Cu <sub>2</sub> O 9.0m/o (4.5w/o)	117.0	312	A6
60	63.6	79.6	21.8	8.5			12.2	6.3			Bi <sub>2</sub> O <sub>3</sub> 2.4m/o (5.6w/o)	132.0	301	A6
61	63.6	75.0	21.8	8.0			9.3	4.0			Bi <sub>2</sub> O <sub>3</sub> 5.3m/o (13.0w/o)	128.0	315	A6
62	69.2	78.4	20.4	7.2			9.4	2.1			Bi <sub>2</sub> O <sub>3</sub> 5.2m/o (12.3 w/o)	126.0	315	A6
63	61.1	80.4	21.8	9.0			14.6	7.0			PbF <sub>2</sub> 2.5m/o (3.6w/o)	144.0	300	A6
64	56.0	73.3	21.8	8.9			14.6	7.0			PbF <sub>2</sub> 7.5m/o (10.9w/o)	119.0	297	A6
65	45.0	75.0	24.0	12.5					31.0	12.5		137.0	277	A6
66	42.1	73.0	22.2	12.0					35.7	15.0		57.0		A7
67	39.5	71.0	21.4	12.0					39.1	17.0		65.0		A7
68	53.8	80.0	32.3	15.0					13.9	5		46.5		A7
69	45.6	75.0	29.3	15.0					25.1	10		92.5		A7
70	42.1	72.5	27.9	15.0					30.0	12.5		67.5		A7
71	38.9	70.0	26.7	15.0					34.4	15.0		57.0		A7
72	42.7	72.5	33.0	17.5					24.3	10.0		61.5		A7
73	39.4	70.0	31.6	17.5					29.1	12.5		97.0		A7
74	46.9	75.0	40.1	20.0					12.9	5		51.0		A7
75	39.9	70.0	36.6	20.0					23.6	10		78.5		A7
76	34.0	65.0	33.6	20.0					32.4	15		47.5		A7
77	17.5	37.22			65.0	37.2					BaO - 17.4m/o (25.6w/o)	70.5		A7
78	20	40.1			60.0	32.4					BaO - 20.0m/o (27.6w/o)	82.41		A8
79	20	39.0			56.7	29.8					BaO - 23.3m/o (31.2w/o)	89.22		A8
80	22.5	42.6			55.0	28.1					BaO - 22.5m/o (29.3w/o)	93.56		A8
81	22.5	44.9			50.0	24.2					BaO - 25.0m/o (30.9w/o)	95.65		A8

\*No temperature range given.

TABLE A4

## Lead Free Alumina Glasses

Glass No.	$Al_2O_3$		$B_2O_3$		$SiO_2$		$MgO$		Other	$\bar{\alpha}$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o			
82	2.4	4.0	3.3	3.8	94.0	92.0			Na <sub>2</sub> O -0.2m/o (0.2w/o)	9.0*	A9
83		4.8		4.5		81.6			4.6Ba, 4.5Ca	20.0*	A9
84	3.6	6.0	5.1	5.7	91.0	88.0			Na <sub>2</sub> O -0.3m/o (0.3w/o)	12.0*	A9
85		5.5		7.4		85.8			0.6Ba, 0.7Na	15.0*	A9
86		5.0		8.8		83.6			1.2Ba, 1.4Na	21.0*	A9
87		4.2		9.1		85.9			0.3Ba, 0.5Ca	12.0*	A9
88	3.2	5.2	8.9	10.0	86.8	83.9			CaO -1.1m/o (1.0w/o)	15.0*	A9
89	0.8	1.4	9.6	10.9	89.6	87.7				14.0*	A9
90	3.0	4.9	10.7	12.0	86.3	83.1				10.0*	A9
91	1.7	2.8	10.8	12.2	87.5	85.0				16.0*	A9
92	2.4	4.0	11.2	12.5	86.4	83.5				13.0*	A9
93	7.7	12.2	13.7	13.8	78.5	73.0				21.0*	A9
94	2.5	4.0	14.0	17.5	77.6	74.5			CaO -5.5m/o (4.0w/o)	23.0*	A9
95	2.5	4.0	15.7	17.5	81.8	78.5				18.0*	A9
96	0.7	1.1	18.3	20.5	81.1	78.4				23.0*	A9
97	0.8	1.3	27.2	30.0	72.0	68.5				30.0*	A9
98		14.5		10.0	56.2	54.0	7.0	4.5	CaO -19.0m/o (17.0w/o)	36.2*	A10
99		17.0		5.0		62.0		7.0	8.0Ca, 1.0Na	42.0	A3c
100		15.0		5.0		57.0			6.0Ba, 10Ca	46.0	A3d
101		1.0		26.0		71.0			1.0K, 1.0Li	32.0	A3e
102	0.2	0.3	2.6	3.0	97.2	96.0				8.0	A3f
103		6.0		24.0		66.0			1.0Li, 1.0F <sup>-</sup> , 2.0Na	39.0	A3g
104	13.0	22.6			53.0	54.3	34.0	23.1		48.2	A8
105	12.0	21.1			52.0	53.8	36.0	25.1		50.0	A8
106	14.0	24.2			51.0	51.9	35.0	23.9		49.0	A8
107	13.0	22.8			50.0	51.5	37.0	25.7		49.0	A8
108	11.0	19.6			50.0	52.7	39.0	27.7		51.0	A8
109	9.0	16.5			50.0	53.9	41.0	29.6		53.1	A8
110	13.0	22.9			48.0	49.9	39.0	27.2		50.9	A8
111	11.0	19.8			48.0	51.0	41.0	29.2		51.9	A8
112	9.0	16.6			48.0	52.1	43.0	31.3		53.6	A8
113	13.0	28.1			46.0	48.1	41.0	28.8		51.5	A8
114	11.0	20.0			46.0	49.1	43.0	30.9		53.3	A8
115	9.0	16.7			46.0	50.2	45.0	33.1		57.5	A8
116	13.0	23.3			44.0	46.3	43.0	30.4		53.3	A8
117	11.0	20.1			44.0	47.4	45.0	32.5		55.6	A8
118	9.0	16.8			44.0	48.5	42.0	34.7		--	A8
119	10.9	18.8			52.3	53.0	31.8	21.5	TiO <sub>2</sub> -5.0m/o (6.7w/o)	43.7*	A10
120	6.2	11.1			48.0	50.8	24.0	16.9	CaO -21.9m/o (21.6w/o)	42.0*	A10
121		12.8				60.1		3.3	16.5Ca, 7.2Ti	32.0*	A10
122	12.1	20.0			57.6	56.0	23.2	15.0	TiO <sub>2</sub> -6.9m/o (9.0w/o)	--	A3h

\* No temperature range given.



TABLE A5(a)  
Other Lead Free Glasses

Glass No.	B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		BaO		Bi <sub>2</sub> O <sub>3</sub>		TiO <sub>2</sub>		Other	$\bar{\alpha}$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o			
123			0.0	0.0			100.0	100.0				151.0*	A12
124			7.5	6.5			92.5	93.5				131.7*	A12
125			11.4	10.0			88.6	90.0				118.1*	A12
126			16.8	14.8			83.2	85.2				111.4*	A12
127			27.2	24.4			72.8	75.6				87.0*	A12
128			41.6	38.0			58.4	62.0				71.9*	A12
129			49.2	45.5			50.8	54.5				75.6*	A12
130			55.9	52.2			44.1	47.8				49.8*	A12
131			60.8	57.2			39.2	42.8				47.5*	A12
132			71.5	68.4			28.5	31.6				26.0*	A9
133			91.3	90.0			8.7	10.0				15.0*	A9
134			100.0	100.0			0.0	0.0				4.87*	A12
135	18.8	10.1			37.5	44.4	6.2	22.4	37.4	23.1	CaF <sub>2</sub> -4.7m/o (2.9w/o)	91.0*	A13
136	17.9	9.8			35.7	43.1	5.9	21.8	35.7	22.5	CaF <sub>2</sub> -7.7m/o (4.8w/o)	111.3*	A13
137	17.3	9.6			34.7	42.3	5.8	21.4	34.5	22.0	CaF <sub>2</sub> -14.3m/o (9.1w/o)	114.2*	A13
138	16.1	9.2			32.2	40.4	5.3	20.4	32.1	21.0	ZrO <sub>2</sub> -3.0m/o (2.9w/o)	114.0*	A13
139	18.2	9.8			36.3	43.1	6.0	21.8	36.4	22.5	ZrO <sub>2</sub> -5.0m/o (4.8w/o)	92.0*	A13
140	17.8	9.6			35.7	42.3	5.9	21.4	35.5	22.0		93.0*	A13
141	13.4	5.2			33.3	28.4	20.0	51.7	33.3	14.8		--	A13
142	12.5	5.0			31.2	27.6	18.7	50.2	31.2	14.4	CaF <sub>2</sub> -6.4m/o (2.9w/o)	77.2*	A13
143	12.8	5.0			32.0	27.6	19.1	50.2	32.0	14.4	ZrO <sub>2</sub> -4.2m/o (2.9w/o)	97.8*	A13
144	12.4	4.9			31.0	27.0	18.6	49.2	31.1	14.1	ZrO <sub>2</sub> -6.9m/o (4.8w/o)	95.2*	A13
145	6.8	2.3			33.3	24.7	26.6	60.1	33.3	12.9		94.0*	A13
146	6.2	2.2			30.9	24.0	24.7	58.4	30.8	12.5	CaF <sub>2</sub> -7.4m/o (2.9w/o)	103.0*	A13
147	6.4	2.2			31.7	24.0	25.4	58.4	31.7	12.5	ZrO <sub>2</sub> -4.8m/o (2.9w/o)	100.2*	A13
148	6.0	2.1			30.8	23.6	24.6	57.3	30.8	12.3	ZrO <sub>2</sub> -7.8m/o (4.8w/o)	81.6*	A13
149	20.1	9.1			33.3	33.2	13.3	40.4	33.3	17.3		107.9*	A13
150	18.2	8.6			30.3	31.6	12.1	38.5	30.3	16.5	CaF <sub>2</sub> -9.0m/o (4.8w/o)	87.3*	A13
151	19.3	8.8			32.2	32.3	12.8	39.2	32.1	16.8	ZrO <sub>2</sub> -3.6m/o (2.9w/o)	89.1*	A13
152	18.8	8.6			31.3	31.6	12.6	28.5	31.4	16.5	ZrO <sub>2</sub> -5.9m/o (4.8w/o)	89.3*	A13
153	26.7	14.6			33.3	40.1	6.7	24.4	33.3	20.9		82.3*	A13
154	25.4	14.1			31.8	39.0	6.4	23.7	31.8	20.3	CaF <sub>2</sub> -4.7m/o (2.9w/o)	84.2*	A13
155	24.7	13.9			30.8	38.2	6.2	23.2	30.7	19.9	CaF <sub>2</sub> -7.6m/o (4.8w/o)	73.5*	A13

\* No temperature range given.



TABLE A5(b)

## Other Lead Free Glasses

Glass No.	$B_2O_3$		$SiO_2$		$ZnO$		$CdO$		$La_2O_3$		$\bar{\alpha}$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o		
156	79.0	44.6							21.0	55.4	72.5	A14
157	75.0	39.1							25.0	60.9	75.4	A14
158	72.0	35.5							28.0	64.5	--	A14
159	63.5	36.7					14.6	13.2	21.9	50.1	78.9	A14
160	61.2	31.1					15.3	14.3	23.0	54.6	--	A14
161	69.0	40.8					15.6	16.7	15.4	42.5	73.1	A14
162	55.6	27.7					22.2	20.4	22.2	51.9	--	A14
163	66.7	41.8					22.2	25.7	11.1	32.6	70.3	A14
164	57.1	32.3					28.6	29.9	14.3	37.9	82.4	A14
165	47.9	24.8					34.7	33.1	17.4	42.1	--	A14
166	64.3	42.8					28.6	35.1	7.1	22.1	68.0	A14
167	50.0	29.3					40.0	43.3	10.0	27.4	87.7	A14
168	45.4	25.6					43.7	45.5	10.9	28.9	94.6	A14
169	59.5	39.5					34.7	42.5	5.8	18.0	73.9	A14
170	48.8	33.7					40.0	46.6	6.6	19.6	81.2	A14
171	60.1	29.7					43.8	49.1	7.4	21.1	86.9	A14
172	56.3	44.9					39.9	55.1			64.2	A14
173	50.1	41.1					43.7	58.9			72.3	A14
174	45.4	35.2					49.9	64.8			77.0	A14
175	63.4	31.1					54.6	68.9			--	A14
176	63.0	36.3					22.2	23.6	14.9	40.1	76.9	A14
177	60.7	37.1					28.6	32.3	10.7	30.6	76.1	A14
178	43.6	26.2					49.9	55.4	6.5	18.4	91.8	A14
179	40.0	36.3			60.0	63.7					37.4	A11
180	32.0	29.3	8.0	6.3	60.0	64.3					32.1	A11
181	30.0	27.6	10.0	7.9	60.0	64.5					36.5	A11
182	20.0	18.6	20.0	16.1	60.0	64.3					33.7	A11
183	44.8	41.0			55.2	59.0					37.7	A11
184	45.0	41.2			55.0	58.8					37.1	A11
185	40.0	36.8	5.0	4.0	55.0	59.2					--	A11
186	35.0	32.4	10.0	8.0	55.0	59.6					35.4	A11
187	45.0	41.7	5.0	4.0	50.0	54.2					34.9	A11

## APPENDIX B

### Viscosity Data

#### Explanation of Column Headings for Tables B1 and B2

##### 1. Composition

For most of the glass compositions the concentrations of all constituent oxides are given in both mole percent (m/o) and weight percent (w/o). For a few of the multi-component glasses in Table B2, the concentrations of the major constituents are given in weight percent only, and the minor constituents' concentrations are given in the "Other" column as weight percent of the oxide of the element listed.

##### 2. $T_{st}$ through $T_m$

The nine columns beginning with  $T_{st}$  list the temperature in  $^{\circ}\text{C}$  at which the glass composition has the viscosity in Pa·s given at the top of the column. Six of the nine columns are the named viscosity reference points given in Table 2.

##### 3. References

- B1. J. Gallup and A. G. F. Dingwall, "Properties of Low-Temperature Solder Glasses," Am. Ceram. Soc. Bull., 36 (2), 47-51 (1957).
- B2. B. A. Pospelov, "The Viscosity of the Binary Lead Silicate, Lead Borate and Lead Phosphate Glasses in the Temperature Interval between Softening and Annealing," Zhur. Fiz. Khim., 33, 543-46 (1950).
- B3. Material Information for Corning Code 7570, Corning Glass Works, Corning, N. Y., August 1976. (See reference B4 for composition data).

- B4. Handbook of Tables for Applied Engineering Science, R. E. Bolz and G. T. Tuve eds., pp 123-26, Chemical Rubber, Cleveland, OH (1970).
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- B6. R. L. Myuller, "Nature of the Energy of Activation, and Experimental Data on the Fluidity of Refractory Glass-Forming Substances," J. Appl. Chem. USSR, 28 (4), 339-45 (1955).
- B7. T. Ejima and M. Kameda, "Viscosity of Liquid Lead Silicate and Lead Borate," J. Jap. Inst. Metals, 31, 120-25 (1967).
- B8. H. Tweer, N. Laberge and P. B. Macedo, "Inadequacies of Viscosity Theories for a Bitreous KNO<sub>3</sub>-Ca (NO<sub>3</sub>)<sub>2</sub> Melt," J. Am. Ceram. Soc., 54 (2), 121-23 (1971).
- B9. R. L. Green, "X-Ray Diffraction and Physical Properties of Potassium Borate Glasses," J. Am. Ceram. Soc., 25 (3), 83-89 (1942).
- B10. R. Brueckner and J. F. Navarro, "Phisiochemical Investigations in the System B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>," Glastech. Ber., 39 (6), 283-93 (1966).
- B11. T. Shartsis and S. Spinner, "Viscosity and Density of Molten Optical Glasses," J. Res. NBS, 46 (3), 176-94 (1951).
- B12. A. Prabhu, G. L. Fuller, R. L. Reed and R. W. Vest, "Viscosity and Surface Tension of a Molten Lead Borosilicate Glass," J. Am. Ceram. Soc., 58 (3-4), 144-45 (1975).
- B13. This work. See Section IIIB2.



TABLE B1

## Lead Glasses

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		T <sub>st</sub> 10 <sup>13.5</sup>	T <sub>a</sub> 10 <sup>12</sup>	T <sub>d</sub> 10 <sup>10.5</sup>	T <sub>s</sub> 10 <sup>6.6</sup>	T <sub>5</sub> 10 <sup>5</sup>	T <sub>4</sub> 10 <sup>4</sup>	T <sub>w</sub> 10 <sup>3</sup>	T <sub>2</sub> 10 <sup>2</sup>	T <sub>1</sub> 10 <sup>1</sup>	Ref.
	m/o	w/o	m/o	w/o	m/o	w/o	m/o	w/o										
1	50	76.2	50	23.8					365.5	376.5	393.5	435						B1
2	60	82.8	40	17.2					317	327	344	383						B1
3	69.5	88	30.5	12					272.5	281.5	296	330						B1
4	45	72.4	55	27.6					380.3	403	417	460						B2
5	35	63.3	65	36.7					426.3	434	452	496						B2
6	20	48.2			80	51.8			489	535	583	745						B5
7	30	61.4			70	38.6			458.5	492	530	659	737					B5
8	33.3	65			66.7	35			444	476	511.5	632	703	770	856			B5
9	35	66.7			65	33.3			442	473	509.5	624	702	773	870			B5
10	40.1	71.3			59.9	28.7			427.5	455	488	595	653	707	794			B5
11	42.1	73			57.9	27			403	429.5	460	555	614	668	704			B5
12	45	75.2			55	24.8			398	424	454.5	562						B5
13	48	77.4			52	22.6			378.5	402	428	508						B5
14	50	78.8			50	21.2			381	400	424.5	497						B5
15	55	81.9			45	18.1			351.5	373	397	469						B5
16	60	84.8			40	15.2			347	367	389.5	456						B5
17	63	86.3			37	13.7			341.5	359	378.5	439						B5
18	66.6	88.1			33.4	11.9			331.5	346	362	422						B5
19	70	89.7			30	10.3			338	354	371	427						B5
20	73	90.9			27	9.1			318	333	350.5	404						B5
21	40	71.2			60	28.8			421.5	444	481	568						B1
22	60	84.8			40	15.2			344.5	375.5	379	429						B1
23	45	75.2			55	24.8			389	417	441.3	514						B2
24	35	66.7			65	33.3			441.3	468	499	589						B2
25	50	78.8			50	21.2						479	508	535	578	662	780	B6
26	42.4	73.2			57.6	26.8									802	915	1130	B7
27	44.3	74.7			55.7	25.3									763	857	1041	B7
28	47.6	77.1			52.4	22.9									791	967		B7
29	42.7	72.06	26.5	13.95	30.8	13.99			393.5	406.5	427	477						B1
30	62	84.95	17.6	7.52	20.4	7.53			300	311	329	371						B1
31	33.56	63	42.69	25	23.75	12												B12
32	33.56	63	42.69	25	23.75	12				446	465	(524)						B12
33	30.51	58	38.78	23	21.49	11	9.21	8		452	470	(537)						B13
34	51.55	75	24.23	11	7.66	3	16.55	11	342	363		440						B3
35	58.91	82	23.03	10	13.34	5	4.72	3	300	315		380						B4



TABLE B2

## Lead Free Glasses

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Other	T <sub>st</sub> 10 <sup>13.5</sup>	T <sub>a</sub> 10 <sup>12</sup>	T <sub>d</sub> 10 <sup>10.5</sup>	T <sub>s</sub> 10 <sup>6.6</sup>	T <sub>5</sub> 10 <sup>5</sup>	T <sub>4</sub> 10 <sup>4</sup>	T <sub>w</sub> 10 <sup>3</sup>	T <sub>2</sub> 10 <sup>2</sup>	T <sub>m</sub> 10 <sup>1</sup>	Ref.
	m/o	w/o	m/o	w/o	m/o	w/o											
36			100					253	275	298	376	431	482	553	670	977	B8
37			100					210	232	255	267						B9
38			98	98.3	2	1.7		(237)*	257	275	364	427	485	560	710	1025	B10
39			94	94.3	6	5.2		(243)	264	282	380	445	505	590	760	1105	B10
40			90	91.25	10	8.75		(248)	270	292	395	467	527	615	795		B10
41			80	82.26	20	17.74		(257)	284	310	440	530	615	730	930		B10
42			70	73	30	27		(275)	310	345	512	630	750	940			B10
43			60	63.5	40	36.5		(287)	327	375	587	757	920	1155			B10
44			55	58.6	45	41.4		(298)	343	405	680	875	1035				B10
45				26		71	1Al, .5Li, .5Na, 1K	455	495					1070			B4
46				5		62	17Al, 8Ca, 1Na, 7Mg	670	715		915			1190			B4
47				5		57	15Al, 6Ba, 7Mg, 10Ca	670	710		910			1175			B4
48				24		66	6Al, 2Na, 1U, 1F	410	450		705						B4
49		0.2		10.7		38.3	2.9Al, 42.8Ba, 4.5Ca .4As, .25b					826	894	981	1109	1300	B11
50		0.2		6.7		38.2	4.9Al, 42.8Ba, 4.2Zn 2.3Ca, .4As, .2Sb					844	904	974	1076	1236	B11
51		1.4		4.4		37.2	4.9Al, 44.8Ba, 5.6Zn .6Na, .3As, .7Sb						903	981	1086	1271	B11
52				11.4		37.8	44.2Ba, 3.6Ca, 2.3Be .2Zr, .3As, .2Sb						879	937	1015	1134	B11



## A. ABOU-EL-AZM &amp; H. A. EL-BATAL: SOFTENING POINTS OF GLASSES RICH IN PbO

<sup>B3</sup>  
Table 1—continued

Composition (wt. %)		Added oxide	Softening point (°C)
SiO <sub>2</sub>	PbO		
		ZnO	
25-22	74-57	0-21	528
25-40	74-18	0-42	531
26-12	72-89	1-07	536
27-17	70-57	2-26	566
		CaO	
25-20	74-54	0-26	528
25-39	74-10	0-51	536
25-98	72-72	1-30	550
27-03	70-26	2-75	586
		SrO	
25-12	74-42	0-46	528
25-27	73-80	0-93	534
25-71	71-93	2-36	547
26-42	68-71	4-87	576
		BaO	
25-07	74-18	0-75	527
25-17	73-45	1-38	533
25-38	71-12	3-50	546
25-84	67-07	7-09	570
		B <sub>2</sub> O <sub>3</sub>	
24-11	75-31	0-58	523
23-21	75-62	1-17	492
20-44	76-60	2-96	456
15-65	78-30	6-05	422
		Al <sub>2</sub> O <sub>3</sub>	
24-06	75-08	0-85	536
23-08	75-21	1-71	539
20-14	75-50	4-36	548
15-23	76-12	8-65	563
		TiO <sub>2</sub>	
23-90	74-73	1-37	525
22-83	74-53	2-64	532
19-68	73-77	6-55	554
		ZrO <sub>2</sub>	
23-77	74-25	1-98	546
22-52	73-41	4-07	563
21-33	72-75	5-92	589

The softening points of the lead borate glasses decreased as the lead oxide content increased, and were lowered still further when the lead oxide was replaced by alkalis; when the lead oxide was replaced by divalent metal oxides the softening points were raised. The replacement of boric oxide, cation for cation, by alumina lowered the softening point in proportion to the amount introduced; the replacement of boric oxide by a tetravalent metal oxide raised the softening point, the glasses containing zirconia having higher softening point than the glasses containing titania.

<sup>B4</sup>  
Table 2. Softening points of lead borate glasses and glasses derived from them

Composition (wt. %)		Added oxide	Softening point (°C)
B <sub>2</sub> O <sub>3</sub>	PbO		
40-39	59-61	—	508
39-36	60-64	—	501
37-97	62-03	—	495
37-09	62-91	—	489

<sup>B4</sup>  
Table 2—continued

Composition (wt. %)		Added oxide	Softening point (°C)
B <sub>2</sub> O <sub>3</sub>	PbO		
36-22	63-78	—	484
35-39	64-61	—	480
34-27	65-73	—	477
32-78	67-22	—	473
32-17	67-83	—	470
30-87	69-13	—	465
30-26	69-74	—	461
29-11	70-89	—	457
28-07	71-93	—	453
27-09	72-91	—	449
25-97	74-03	—	443
25-55	74-45	—	438
23-78	76-22	—	429
22-71	77-29	—	420
21-73	78-27	—	410
21-16	78-84	—	399
20-18	79-82	—	389
18-76	81-24	—	380
18-01	81-99	—	372
16-86	83-14	—	364
15-77	84-23	—	357
15-54	84-46	—	349
13-96	86-04	—	341
		Li <sub>2</sub> O	
25-23	74-70	0-07	430
25-49	73-47	0-14	426
		Na <sub>2</sub> O	
25-25	74-67	0-18	428
25-40	74-28	0-32	424
		K <sub>2</sub> O	
25-20	74-60	0-20	427
25-40	74-18	0-42	423
		MgO	
25-21	74-61	0-18	432
25-40	74-23	0-37	436
26-07	72-99	0-74	443
27-24	70-80	1-96	461
		ZnO	
25-17	74-46	0-37	431
25-33	73-67	0-74	432
25-82	72-30	1-88	435
26-70	69-40	3-90	439
		CaO	
25-19	74-56	0-25	433
25-37	74-13	0-50	435
25-98	72-72	1-30	441
27-04	70-25	2-71	454
		SrO	
25-13	74-40	0-47	432
25-26	73-81	0-93	434
25-69	71-93	2-38	439
26-42	68-70	4-88	451
		B <sub>2</sub> O	
25-09	74-22	0-69	432
25-14	73-36	1-50	434
25-40	71-10	3-50	438
25-80	67-10	7-10	444
		Al <sub>2</sub> O <sub>3</sub>	
23-90	74-70	1-40	432
22-73	74-40	2-87	435
19-58	73-28	7-14	437
14-30	71-70	14-00	440



B4  
Table 2-continued

Composition (mole. %)		Added oxide	Softening point (°C)
B <sub>2</sub> O <sub>3</sub>	PbO		
TiO <sub>2</sub>			
23.74	73.94	2.32	441
22.86	73.00	4.44	451
18.81	70.40	10.79	464
ZrO <sub>2</sub>			
24.85	74.80	0.35	439
24.68	74.60	0.72	440
24.53	74.43	1.04	441
24.20	74.04	1.76	443
24.42	73.13	3.45	447

*Discussion*

The changes in the softening points produced by replacing lead oxide by one of the alkali oxides depends partly on the ionic radius of the cation introduced and partly on its field strength, together with the changes in the mobilities of the resulting atomic groups. The softening points are higher for the glasses containing large cations such as K<sup>+</sup> because the relative compactness of the structure reduces the mobility of these groups much more than that of the groups containing smaller cations such as Na<sup>+</sup> or Li<sup>+</sup>.

The replacement of lead oxide by oxides of the divalent metals caused changes in the softening points which can be related mainly to the field strengths of the cations and also to their sizes.

The introduction of a trivalent or tetravalent metal oxide causes changes in the softening point which depend mainly on the strength of the bond between the cations introduced and the oxygens to which they are linked to create network forming units.

*Alkali borate glasses**Results*

The softening point increased rapidly when small amounts of alkalis (up to 0.2 mole R<sub>2</sub>O per mole B<sub>2</sub>O<sub>3</sub>) were added to boric oxide glass; with further additions, the softening point increased, but at a much slower rate. Lithium caused the greatest change, and potassium the smallest with sodium between. The addition of alumina to sodium borate glasses caused the softening point to increase at a much slower rate, while the addition of magnesia or zinc oxide raised the softening points.

B5  
Table 2-continued  
Softening points of alkali borate glasses and glasses derived from them

Composition (mol. %)				Softening point (°C)
B <sub>2</sub> O <sub>3</sub>	R <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	RO	
Na <sub>2</sub> O				
Pure boric oxide glass	—	—	—	355
95.74	4.26	—	—	406
91.82	8.18	—	—	418

B5  
Table 2-continued

Composition (mol. %)				Softening point (°C)
B <sub>2</sub> O <sub>3</sub>	R <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	RO	
91.00	9.00	—	—	433
89.99	10.01	—	—	443
88.73	11.27	—	—	456
87.08	12.72	—	—	468
84.89	15.11	—	—	488
81.79	18.21	—	—	507
79.73	20.27	—	—	515
77.12	22.88	—	—	522
73.75	26.25	—	—	518
63.52	36.48	—	—	511
<i>K<sub>2</sub>O</i>				
93.67	6.33	—	—	404
88.09	11.91	—	—	416
86.93	13.07	—	—	428
85.53	14.47	—	—	438
83.80	16.20	—	—	449
81.60	18.40	—	—	466
78.71	21.29	—	—	484
74.73	25.27	—	—	498
72.12	27.88	—	—	503
69.92	30.08	—	—	510
64.89	35.11	—	—	513
59.65	40.35	—	—	500
<i>Li<sub>2</sub>O</i>				
97.21	2.79	—	—	412
94.57	5.43	—	—	424
94.01	5.99	—	—	446
93.30	6.70	—	—	461
92.42	7.58	—	—	480
91.27	8.73	—	—	498
89.70	10.30	—	—	508
87.44	12.56	—	—	528
85.91	14.09	—	—	534
83.93	16.07	—	—	548
81.33	18.67	—	—	552
<i>Na<sub>2</sub>O</i> <i>Al<sub>2</sub>O<sub>3</sub></i>				
86.04	1.66	6.30	—	445
85.42	8.45	6.26	—	450
84.42	9.40	6.18	—	462
83.31	10.59	6.10	—	470
81.86	12.14	6.00	—	481
79.92	14.23	5.85	—	493
77.17	17.18	5.65	—	509
73.07	21.58	5.35	—	536
65.93	29.24	4.83	—	521
<i>ZnO</i>				
80.94	7.21	11.85	—	452
80.39	7.84	11.77	—	460
79.51	8.84	11.65	—	469
78.52	10.98	11.50	—	480
77.23	11.46	11.31	—	489
75.50	13.44	11.06	—	494
73.04	16.26	10.70	—	516
69.36	19.48	10.16	—	534
62.89	27.90	9.21	—	518



A. ABOU-EL-AZM & H. A. EL-BATAL : SOFTENING POINTS OF GLASSES RICH IN  $\text{PbO}$ 

Table 35 continued

Composition (mol. %)				Softening point (°C)
$\text{B}_2\text{O}_3$	$\text{R}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{RO}$	
82.92	7.39	—	9.69	500
82.35	8.02	—	9.63	503
81.52	9.95	—	9.53	514
80.48	10.11	—	9.41	519
79.13	11.62	—	9.25	528
77.22	13.75	—	9.03	539
74.66	16.61	—	8.73	545
70.82	21.90	—	8.28	531
64.08	28.43	—	7.49	521
				$\text{MgO}$
89.44	7.97	—	2.59	470
88.77	8.75	—	2.58	486
87.81	9.64	—	2.55	500
86.61	11.88	—	2.51	518
84.94	12.60	—	2.46	526
82.85	14.75	—	2.40	538
79.90	17.78	—	2.32	554
75.52	22.29	—	2.19	536
67.91	30.12	—	1.97	525
80.90	14.41	—	4.69	576
78.09	17.38	—	4.55	565
73.90	21.81	—	4.29	549
66.60	29.54	—	3.86	522

## Discussion

The formation of  $\text{BO}_4$  groups on the addition of an alkali to boric oxide increases the viscosity and hence the softening point of the glass. This rapid increase continues till one fifth of the boron atoms are four-coordinated, after which any increase in the alkali content decreases the mobility of the groups and hence increases the softening point.

The effect of the different alkali ions can be related to the compactness of the structure. In these glasses the rings formed by  $\text{BO}_3$  and  $\text{BO}_4$  groups are small and hence  $\text{Li}^+$  ions (small co-ordination and high field strength) give higher softening points,  $\text{Na}^+$  ions give intermediate softening points, and  $\text{K}^+$  ions give the lowest softening points.

The formation of  $\text{AlO}_4$  groups when alumina is introduced takes precedence over the formation of  $\text{BO}_4$ , and more sodium is therefore needed to complete the four co-ordination of one fifth of the boron when alumina is present. Magnesia and zinc oxide take part, at least to some degree, in the four-co-ordination of the boron by providing the necessary oxygen and the  $\text{Mg}^{2+}$  or  $\text{Zn}^{2+}$  ions become enclosed within the interstices in the structure.

## Cabal glasses

## Results

The softening point was raised when boric oxide in the base glass was replaced by lime or alumina, the effect of alumina being greater than that of lime. The replacement of lime, cation for cation, by a monovalent

metal oxide lowered the softening point. The effect was greatest in glasses containing lithium and least in glasses containing potassium, with the glasses containing sodium between. The replacement of lime, cation for cation, by a divalent metal oxide lowered the softening point while the tetravalent metal oxides increased the softening point in the order silica (highest), zirconia, titania, when replacing boric oxide.

Table 36 Softening points of Cabal glasses and glasses derived from them

Composition (mol. %)				Softening point (°C)
$\text{B}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	Added oxide	
40.03	30.03	29.84	—	683
34.06	29.09	36.85	—	693
28.22	28.32	43.46	—	710
37.00	31.60	31.40	—	720
				$\text{Li}_2\text{O}$
40.26	30.20	29.48	0.36	693
41.33	31.02	25.81	1.84	667
42.70	32.10	21.48	3.82	643
44.26	33.22	16.60	8.92	620
45.90	34.43	11.48	13.19	583
47.70	35.80	5.90	10.60	56
49.60	37.20	—	13.20	580
				$\text{Na}_2\text{O}$
40.21	30.19	29.45	0.55	694
40.96	30.71	25.56	2.83	673
41.90	31.40	20.91	8.79	648
42.88	32.20	16.06	13.86	627
43.90	32.97	10.98	12.15	593
45.05	33.80	5.62	18.53	566
46.20	34.66	—	19.14	553
				$\text{K}_2\text{O}$
40.10	30.10	29.00	0.80	694
40.30	30.26	25.21	4.23	680
40.60	30.50	20.30	8.60	65
41.00	30.75	15.35	12.90	634
41.30	31.00	10.33	17.37	598
41.70	31.24	5.21	21.85	569
42.00	31.54	—	26.46	559
				$\text{MgO}$
40.15	30.13	29.10	0.72	692
40.60	30.43	25.35	3.62	698
41.60	31.20	20.77	6.43	705
41.80	31.33	15.65	11.22	711
42.40	31.84	10.60	15.16	718
43.00	32.30	5.38	19.32	725
43.72	32.83	—	23.45	735
				$\text{ZnO}$
39.80	29.90	28.86	3.44	692
39.10	29.36	24.45	7.09	697
38.48	28.72	19.12	13.90	705
				$\text{CaO}$
39.50	29.63	28.61	2.26	687
37.52	28.15	25.60	10.73	675
35.40	26.60	17.70	20.30	666
33.50	25.17	12.57	28.76	657
31.80	23.84	7.93	36.43	648
30.26	22.72	3.78	43.24	638
28.80	21.60	—	49.60	627

B6  
Table A—continued

Composition (wt. %)			Softening point	
B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Added oxide	(°C)
<i>BaO</i>				
39.30	29.52	28.52	2.66	682
36.80	27.63	23.00	12.57	672
34.10	25.57	17.02	23.31	662
31.75	23.84	11.91	32.50	650
29.70	22.28	7.42	40.60	635
27.92	20.95	3.49	47.64	625
26.27	19.71	—	54.02	615
<i>SiO<sub>2</sub></i>				
38.78	29.88	29.68	1.68	692
37.50	29.65	29.45	3.40	700
33.81	29.02	28.83	8.34	712
28.01	28.04	27.85	16.10	727
22.58	27.12	26.94	23.36	758
17.50	26.25	26.10	30.15	794
<i>TiO<sub>2</sub></i>				
38.80	29.87	29.67	1.66	689
37.50	29.65	29.45	3.40	695
33.80	29.02	28.84	8.34	702
<i>ZrO<sub>2</sub></i>				
39.41	29.96	29.76	0.87	689
38.80	29.87	29.67	1.66	692
37.50	29.65	29.45	3.41	679

## Discussion

Changing the proportion of any of the oxides in the Cabal glass (40B<sub>2</sub>O<sub>3</sub>, 30CaO, 30Al<sub>2</sub>O<sub>3</sub>) affects the viscosity and hence the softening point according to the type of replacement, and these effects are governed by the ease of movement of the atomic groups present within the structure. The effect of the monovalent metal oxides depends on the ionic radii of their cations, together with the freedom of mobility of the different ions. Changes of the softening point when any of the divalent metal oxides was introduced may be attributed to the field strength of their cations. Increases in the softening point caused by the introduction of tetra-valent metal oxides is attributed to the relatively higher bond strengths between the cations and oxygens, together with the field strength of the cations.

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## APPENDIX C

### Surface Tension Data

#### Explanation of Column Headings for Tables C1 and C2

##### 1. Composition

For most of the glass compositions the concentrations of all constituent oxides are given in both mole percent (m/o) and weight percent (w/o). For a few of the multi-component glasses the concentrations of the major constituents are given in only weight percent or mole percent, and the minor constituents' concentrations are given in the "Other" column as the corresponding percent of the oxide of the element listed.

##### 2. T and $\gamma$

The column headed T gives the temperature in  $^{\circ}\text{C}$  at which the surface tension in mN/m ( $1 \text{ mN/m} = 1 \text{ dyne/cm} = 1 \text{ erg/cm}^2$ ) is the value given in the column headed  $\gamma$ .

##### 3. $\frac{\Delta\gamma}{\Delta T}$ and $\Delta T$

The column headed  $\Delta\gamma/\Delta T$  gives the change in surface tension, in mN/m, for the temperature change, in  $^{\circ}\text{C}$ , given in the column headed  $\Delta T$ , divided by  $\Delta T$ .

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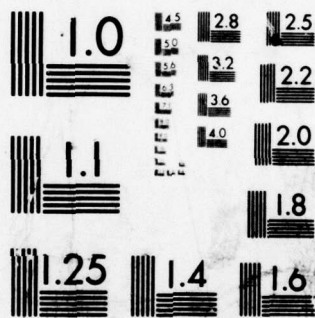
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TABLE C1

## Lead Glasses

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Other	T	Y	$\frac{\Delta y}{\Delta T}$	$\Delta T$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
1	0	0	100	100				800	75.9	.0355	800-1000	C1
2	1.58	4.9	98.42	95.1				800	75.5	.027	800- 900	C1
3	3.39	10.1	96.61	89.9				800	75.5	.029	800- 900	C1
4	5.85	16.6	94.15	83.4				800	74.5	.038	800-1000	C1
5	7.92	21.6	92.08	78.4				800	76.1	.033	800- 900	C1
6	10.72	27.8	89.28	72.2				800	76.3	.037	800- 900	C1
7	12.5	31.4	87.5	68.6				800	75.5	.046	800- 900	C1
8	14.06	34.4	85.94	65.6				800	75.4	.031	800- 900	C1
9	17.16	39.9	82.84	60.1				800	75.4	.037	800- 900	C1
10	20.27	44.9	79.73	55.1				800	84.8	.043	800- 900	C1
11	21.67	47	78.33	53				800	90.6	.027	800- 900	C1
12	23.13	49.1	76.87	50.9				800	89.4	.022	800- 900	C1
13	24.74	51.3	75.26	48.7				800	104	-.01	800- 900	C1
14	28.67	56.3	71.33	43.7				800	121.8	-.054	800- 900	C1
15	32.7	60.9	67.3	39.1				800	136.8	-.07	800- 900	C1
16	38.14	66.4	61.86	33.6				800	150.6	-.078	700- 900	C1
17	42.95	70.7	57.05	29.3				800	157.7	-.066	600- 900	C1
18	49.02	75.5	50.98	24.5				800	162.6	-.029	700- 900	C1
19	55.52	80	44.48	20				800	164.3	-.015	600- 900	C1
20	58.7	82	41.3	18				800	162.3	-.055	600- 900	C1
21	62.27	84.1	37.73	15.9				800	162.4	.0038	600- 900	C1
22	65.71	86	34.29	14				800	161.6	.011	600- 900	C1
23	69.79	88.1	30.21	11.9				800	160.6	.018	600- 900	C1
24	89.06	96.8			10.94	3.2		1000	142	.055	900-1400	C1
25	83.16	94.83			16.84	5.17		1000	157.7	.028	900-1400	C1
26	72.28	90.64			27.72	9.36		1000	176.5	.025	900-1300	C1
27	63.94	86.82			36.06	13.18		1000	186.5	.035	900-1300	C1
28	59.84	84.7			40.16	15.3		1000	194.6	.029	800-1100	C1
29	57.21	83.24			42.79	16.76		1000	199.4	.036	1000-1300	C1
30	55.93	82.5			44.07	17.5		1000	201.6	.027	700-1300	C1
31	45.61	75.7			54.29	24.3		1000	219.1	.016	900-1300	C1
32	41.98	72.88			58.02	27.12		1000	225.6	.006	900-1300	C1
33	40.54	71.69			59.46	28.31		1000	227.8	.001	1000-1300	C1
34	38.49	69.92			61.51	30.08		1000	231.3	.007	1000-1200	C1
										-.014	1300-1400	C1
35	38.40	69.84			61.60	30.16		1000	230.0	.005	1000-1400	C1
36	36.67	68.26			63.33	32.74		1000	233.7	.002	1000-1400	C1
37	33.42	65.09			66.58	34.91		1000	233	.007	1000-1400	C1
38	85.7	95.7			14.3	4.3		1000	142	.02	900-1200	C3
39	75.9	92.1			24.1	7.9		1000	150	.02	800-1200	C3
40	67.4	88.5			32.6	11.5		1000	164	.02	800-1200	C3
41	59.7	84.6			40.3	15.4		1000	183	.02	800-1200	C3
42	56.1	82.6			43.9	17.4		1000	192	.01	800-1200	C3
43	55.6	82.3			44.4	17.7		1000	203	.003	900-1200	C3
44	51.6	79.8			48.4	20.2		1000	209	-.003	800-1200	C3
45	47.7	77.2			52.3	22.8		1000	214	-.003	900-1200	C3

TABLE C1 (Continued)

Glass No.	PbO		B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Other	T	γ	$\frac{\Delta\gamma}{\Delta T}$	ΔT	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
46	50	78.8			50	21.2		900	215	.025	800-1200	C4
47	33.3	64.97			66.7	35.03		500	212	.043	300- 700	C5
48	17.4		76.1				6.5Zn	900	89.2	.05	900-1300	C2
49	18.1		75.1				6.8Zn	900	90.3	.045	900-1300	C2
50	33.56	63	42.69	25	23.75	12		890	155	.07	750- 920	C11
51		62.6		24.4		12.3	.6Bi, 1Al	850	164	.024	795- 968	C10



TABLE C2

## Lead Free Glasses

Glass No.	B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		BaO		Other	T	γ	$\frac{\Delta\gamma}{\Delta T}$	ΔT	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
54	100	100			0	0		900	80.5	.039	900-1100	C6
55	98	95.7			2	4.3		900	80	.042	900-1300	C6
56	97.7	95.1			2.3	4.9		1000	82.5	.041	1000-1300	C6
57	92.3	84.5			7.7	15.5		900	79.4	.043	900-1300	C6
58	86.9	75.1			13.1	24.9		900	88.1	.046	900-1300	C6
59	83.6	69.9			16.4	30.1		900	115.3	.018	900-1300	C6
60	82.2	67.7			18.8	32.3		1000	116.2	.02	1000-1300	C6
61	80.4	65			19.6	35		900	140.7	-.016	900-1300	C6
62	79.8	64.2			20.2	35.8		900	145.7	-.024	900-1300	C6
63	79.2	63.4			20.8	36.6		900	150.5	-.027	900-1300	C6
64	76.2	59.2			23.8	40.8		900	171.4	-.039	900-1300	C6
65	75.4	58.2			24.6	41.8		1000	174.7	-.037	1000-1300	C6
66	72.7	54.7			27.3	45.3		900	197.2	-.042	900-1300	C6
67	71.1	52.8			28.9	47.2		900	211	-.052	900-1300	C6
68	67.9	49			32.1	51		900	220.6	-.043	900-1300	C6
69	66.7	47.6			33.3	52.4		1000	221.3	-.042	1000-1300	C6
70	63.7	44.4			36.3	55.6		900	239	-.046	900-1300	C6
71	59.5	40			40.5	60		1000	251.2	-.057	1000-1300	C6
72	54.1	34.9			45.9	65.1		1000	263.4	-.068	1000-1300	C6
73	48.4	29.9			51.6	70.1		1000	275.1	-.075	1000-1300	C6
74	43.4	25.8			56.6	74.2		1000	288.9	-.085	1000-1300	C6
75	36.2	20.5			63.8	79.5		1000	321.6	-.093	1000-1300	C6
76	93.2	92.9	5.8	5	1.0	2.1		900	84.9	.035	900-1300	C6
77	84.9	84.1	12.9	11	2.3	4.9		900	93.9	.037	900-1300	C6
78	80.2	77.2	14.9	12.4	4.9	10.4		900	97	.041	900-1300	C6
79	66.2	65	29	24.6	4.8	10.4		900	116	.046	900-1300	C6
80	52.9	52.9	42.3	36.5	4.8	10.6		1000	143.8	.029	1000-1300	C6
81	72.6	65	25.8	12.2	11.6	22.8		900	114	.051	900-1300	C6
82	58.2	52.9	30.1	23.6	11.7	23.5		900	137.3	.019	900-1300	C6
83	44.1	41.4	45.2	36.6	10.6	22		1200	175.2	-.011	1200-1300	C6
84	79.8	67.2	4.1	3.0	16.1	29.8		900	110.1	.03	900-1300	C6
85	71.7	61.2	12.5	9.2	15.8	29.6		1000	118.2	.049	1000-1300	C6
86	67.8	57.7	15.8	11.6	16.4	30.7		1000	132.6	-.067	900-1000	
										.031	1000-1300	C6
										-.044	900-1000	
87	75.4	63.2	7.7	5.6	16.9	31.2		900	124.9	.018	900-1300	C6
88	23	20.4	59.8	45.8	17.3	33.8		1300	241.9			C6
89	47.6	40.2	33.3	24.3	19.1	35.5		1100	178.1	.036	1100-1300	C6
90	71.1	57.4	8.2	5.7	20.7	36.9		1000	158.8	-.017	1000-1300	C6
										-.084	900-1000	
91	55.6	45.9	24	17.1	20.4	37		1000	182.6	-.014	1000-1300	C6
										-.044	900-1000	
92	63.4	51.6	15.8	11.1	20.8	37.3		1000	170.2	-.02	1000-1300	C6
										-.096	900-1000	
93	47.1	39.2	32.6	23.4	20.4	37.4		1000	193.7	0.0	1000-1300	C6
94	71.4	55.3	3.9	2.6	24.7	42.1		1000	184	-.038	1000-1300	C6
95	67.5	52.5	7.9	5.3	24.6	42.2		900	197.6	-.048	900-1300	C6

TABLE C2 (Continued)

Glass No.	B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		BaO		Other	T	Y	$\frac{\Delta y}{\Delta T}$	$\Delta T$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
96	63.4	49.6	12	8.1	24.6	42.3		1000	193.8	-.035	1000-1300	C6
										-.071	900-1000	
97	59.5	46.8	16.1	10.9	24.4	42.3		1000	202.5	-.045	1000-1300	C6
										-.095	900-1000	
98	55.3	43.6	20.1	13.7	24.6	42.7		1000	207.7	-.038	1000-1300	C6
										-.087	900-1000	
99	51.3	40.7	24.3	16.6	24.4	42.7		1100	209.7	-.031	1100-1300	C6
										-.058	900-1100	
100	47.4	37.8	28.2	19.4	24.4	42.8		1100	215.5	-.02	1100-1300	C6
										-.064	900-1000	
101	42.8	34.3	32.8	22.7	24.4	43		1100	221.8	-.013	1100-1300	C6
										-.06	900-1000	
102	39.6	31.9	36.1	25.1	24.3	43		1100	226	-.01	1100-1300	C6
										-.046	900-1100	
103	35.7	28.9	40	27.9	24.3	43.2		1100	236.6	-.015	1100-1300	C6
										-.049	900-1000	
104	35.7	28.9	40.1	28	24.2	43.1		1100	235.1	-.01	1100-1300	C6
										-.034	900-1000	
105	32	26	43.9	30.8	24.1	43.2		1100	241.1	-.015	1100-1300	C6
106	63.1	47.2	8.1	5.2	28.9	47.6		900	221.1	-.046	900-1300	C6
107	59.3	44.6	12	7.8	28.7	47.6		900	227.6	-.051	900-1300	C6
108	55.2	41.7	16.1	10.5	28.7	47.8		1100	220.6	-.037	1100-1300	C6
										-.086	900-1000	
109	47.2	36	24.2	15.9	28.6	48.1		900	243.6	-.04	900-1300	C6
110	39.7	30.5	31.7	21	28.7	48.5		1000	251.6	-.034	1000-1300	C6
										-.087	900-1000	
111	35.8	27.7	35.9	24	28.3	48.3		1000	257.5	-.039	1000-1300	C6
										-.071	900-1000	
112	31.8	24.7	39.9	26.8	28.3	48.5		1100	255.8	-.009	1100-1300	C6
										-.085	900-1100	
113	27.6	21.6	44.1	29.7	28.3	48.7		900	274.9	-.032	900-1300	C6
114	23.8	18.7	47.9	32.4	28.3	48.9		1100	273.4	-.017	1100-1300	C6
										-.046	900-1100	
115	15.8	12.5	55.7	38	28.4	49.5		1100	291.4	-.003	1100-1300	C6
										.034	1000-1100	
116	12.2	9.7	59.7	41	28.1	49.3		1100	302	0	1100-1300	C6
117	7.8	6.2	64	44.1	28.3	49.7		1300	318.4	-	-	C6
118	19.8	15.3	50	33.3	30.2	51.4		1100	286.2	-.01	1100-1300	C6
										-.043	1000-1100	
119	64.4	46.4	3.1	1.9	32.6	51.7		900	229.3	-.044	900-1300	C6
120	61.8	44.7	5.6	3.5	32.5	51.8		900	233.6	-.044	900-1300	C6
121	59.4	43.2	8.4	5.3	32.2	50.5		900	238.7	-.046	900-1300	C6
122	58.3	42.3	9.1	5.7	32.6	52		900	239.6	-.049	900-1300	C6
123	53.5	39.1	14.1	8.9	32.3	52		900	247.7	-.051	900-1300	C6
124	49.6	36.4	18	11.4	32.3	52.2		900	246.3	-.038	900-1300	C6
125	45.8	33.7	21.9	13.9	32.3	52.4		900	256.9	-.052	900-1300	C6
126	41.6	30.7	25.9	16.5	32.5	52.8		900	264.2	-.05	900-1300	C6
127	35.7	26.5	31.8	20.4	32.5	53.1		900	271.5	-.04	900-1300	C6
128	32.2	24.1	35.9	23.2	31.9	52.7		900	280.9	-.047	900-1300	C6



TABLE C2 (Continued)

Glass No.	B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		BaO		Other	T	Y	$\frac{\Delta y}{\Delta T}$	$\Delta T$	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
129	25.8	19.4	41.8	27.1	32.3	53.5		1000	282.8	-.033	1000-1300	C6
										-.118	900-1000	
130	20.5	15.5	47.3	30.9	32.2	53.6		1000	287.1	-.02	1000-1300	C6
										-.12	900-1000	
131	16.6	12.6	51.4	33.7	32.1	53.7		1300	292.6	-	-	C6
132	10.7	8.2	57.1	37.7	32.1	54.1		1300	313	-	-	C6
133	33.1	24.3	33.1	21.0	33.8	54.7		900	278.1	-.034	900-1300	C6
134	35.5	25.9	30.1	18.9	34.4	55.2		900	276	-.044	900-1300	C6
135	59.6	41.6	3.8	2.3	36.5	56.1		900	247.8	-.051	900-1300	C6
136	51.2	35.9	11.9	7.2	36.9	56.9		900	257.7	-.047	900-1300	C6
137	47.1	33.2	16.3	9.9	36.6	56.9		900	264.3	-.056	900-1300	C6
138	43.4	30.8	20.1	12.3	36.4	56.9		900	269	-.051	900-1300	C6
139	39.5	28.1	24.1	14.8	36.4	57.1		900	275.1	-.051	900-1300	C6
140	35.4	25.3	28.1	17.3	36.5	57.4		1000	274.8	-.043	1000-1300	C6
										-.072	900-1000	
141	31.8	22.8	31.8	19.7	36.4	57.5		1000	279.5	-.038	1000-1300	C6
										-.072	900-1000	
142	27.9	20.1	36	22.4	36.2	57.5		1000	285.5	-.042	1000-1300	C6
										-.085	900-1000	
143	24.3	17.4	38.5	23.8	37.2	58.8		1200	290.1	-	-	
144	24	17.4	39.8	24.9	36.2	57.7		1000	288.8	-.038	1000-1300	C6
										-.073	900-1000	
145	37.3	26.3	25	15.2	37.7	58.5		1000	276	-.05	1000-1300	C6
										-.074	900-1000	
146	16.7	12.2	47.3	29.8	36	58		1100	304.7	-.035	1100-1300	C6
147	8.4	6.2	55.5	35.3	36.1	58.5		1300	325.6	-	-	C6
148	51.7	35.7	9.9	5.9	38.4	58.4		900	265.6	-.057	900-1300	C6
149	55.5	37.4	3.8	2.2	40.7	60.4		1000	257.6	-.061	1000-1300	C6
150	51.5	34.9	7.9	4.6	40.6	60.5		900	268.3	-.06	900-1300	C6
151	47.7	32.4	11.8	6.9	40.6	60.7		900	272.6	-.058	900-1300	C6
152	43.6	29.8	15.9	9.4	40.4	60.8		900	277.8	-.059	900-1300	C6
153	39.4	27	20.1	11.9	40.5	61.1		900	284.1	-.058	900-1300	C6
154	31.3	21.6	28.3	16.9	40.4	61.5		900	295.4	-.054	900-1300	C6
155	26.3	18.3	33.6	20.2	40.1	61.5		900	304	-.048	900-1300	C6
156	24	16.7	35.8	21.5	40.3	61.8		1000	299.5	-.04	1000-1300	C6
157	20.3	14.2	39.4	23.8	40.3	62		1100	304.3	-.041	1100-1300	C6
158	16.5	11.6	43.5	26.4	40	62		1100	313.5	-.035	1100-1300	C6
159	12.8	9	47	28.6	40.2	62.4		1200	322.1	.033	1200-1300	C6
160	8.2	5.8	51.7	31.6	40.1	62.6		1300	225.5	-	-	C6
161	47.6	31.3	8.1	4.6	44.3	64.1		1000	271.7	-.063	1000-1300	C6
162	43.8	28.9	11.9	6.8	44.3	64.3		1000	270.1	-.048	1000-1300	C6
163	39.5	26.1	15.8	9.0	44.7	64.9		900	288.1	-.062	900-1300	C6
164	31.7	21.1	23.8	13.7	44.5	65.2		900	299.4	-.058	900-1300	C6
165	28.1	18.8	27.7	16	44.2	65.2		900	307.9	-.064	900-1300	C6
166	24	16.1	31.7	18.4	44.3	65.5		1000	305.4	-.054	1000-1300	C6
167	20.3	13.7	35.7	20.8	44	65.5		1100	309	-.046	1100-1300	C6
168	16.1	10.9	39.8	23.3	44.1	65.8		1100	324.4	-.074	1100-1300	C6
169	30.6	19.9	21.9	12.3	47.4	67.8		900	302.7	-.056	900-1300	C6
170	26.5	17.3	26.1	14.7	47.3	68		1000	304.4	-.056	1000-1300	C6
171	23.5	15.4	29.7	16.8	46.9	67.8		1000	311.9	-.054	1000-1300	C6

TABLE C2 (Continued)

Glass No.	B <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		BaO		Other	T	γ	$\frac{\Delta\gamma}{\Delta T}$	ΔT	Reference
	m/o	w/o	m/o	w/o	m/o	w/o						
172	22.1	14.1	27.8	15.3	50.2	70.6		1000	316.9	-.062	1000-1300	C6
173	83.8				10.2		6Al	900	94.4	.05	900-1300	C2
174	82.5				10.1		7.4Al	900	101.1	.046	900-1300	C2
175	85				13.6		1.4Al	900	89.7	.054	900-1300	C2
176	84.7				13.6		1.7Al	900	91.2	.054	900-1300	C2
177	84.3				13.5		2.2Al	900	91.5	.052	900-1300	C2
178	83.5				13.4		3.1Al	900	101.3	.041	900-1300	C2
179	81.7				13.1		5.2Al	900	104.2	.039	900-1300	C2
180	73				11.7		15.3Al	1100	137.6	.04	1100-1300	C2
181	78.5				16.2		5.3Al	900	177.6	.023	900-1300	C2
182	67.9				14		18.1Al	1100	162	.047	1100-1300	C2
183	76.2				23.8			900	171.4	.039	900-1300	C2
184	74.8				23.4		1.8Al	900	172.7	.035	900-1300	C2
185	72				22.4		5.6Al	900	173.6	.013	900-1300	C2
186	95.6				2.4		2K	900	82.6	.043	900-1300	C2
187	90.1				7.9		2K	900	89.8	.043	900-1300	C2
188	85.9				13.5		.6K	900	94.7	.04	900-1300	C2
189	84.9				13.4		1.7K	900	105.4	.03	900-1300	C2
190		10.7		38.3			2.9Al, 4.5Ca, 42.8Ba, 1.4As, .2Sb, .2Pb	1000	286.7	.008	1000-1300	C9
191		4.4		37.3			4.9Al, 5.6Zn, 44.8Ba, .6Na, .3As, 1.4Pb, .7Sb	1000	309.3	.004	1000-1300	C9
192		11.0		37.2			3.5Ca, 41.6Ba, 4.2Be, 2Zr, .5Sb	1000	288.5	.008	1000-1300	C9
193	79.1				14.2		6.7Zn	900	97.8	.033	900-1300	C2
194	77.6				15.8		6.6Zn	900	116.5	.008	900-1300	C2
195	72.8				20.2		7Zn	900	165.7	-.025	900-1300	C2
196	74.7						6.6Zn, 18.7Ca	900	122.1	-.018	900-1300	C2
197	56.1						7.9Zn, 36Ca	1000	232.1	-.04	1000-1300	C2
198	49.4						4.1Zn, 46.5Cd	900	225.7	-.047	900-1300	C2
199		100						900	79.5	.035	800-1300	C7
200		90					10Zn	900	78.4	.043	900-1300	C7
201		50					50Zn	900	79.7	.038	900-1200	C7
202		45					55Zn	900	141.8	.031	900-1300	C7
203		41.4					58.6Zn	900	184.4	.031	900-1300	C7
204		39.2					60.8Zn	900	203.5	.01	900-1300	C7
205		35.4					64.6Zn	900	234.7	.009	900-1300	C7
206		34.4					65.6Zn	1000	242.3	.026	1000-1300	C7
207		29.4					70.6Zn	1000	278.7	.031	1000-1300	C7
208		25.4					74.6Zn	1100	315.2	.033	1100-1300	C7
209	79.2						19.1Sr, 1.7K	1100	119.8	.016	1100-1300	C8
										-.022	900-1100	
210	95.7						1.7K, 2.6Ca	900	84.6	.038	900-1300	C2
211	89.8						2.4K, 7.8Ca	900	86.8	.044	900-1300	C2
212	84.5						2.6K, 12.9Ca	900	92.6	.04	900-1300	C2
213	78						1.1K, 20.8Ca	900	100.4	.018	900-1300	C2



## APPENDIX D

### Contact Angle Data

#### Explanation of Column Headings for Table D1

##### 1. Glass No.

E 1527 is a commercially available frit sold by Drakenfeld Colors.

E 1527B is the E 1527 frit to which 30 weight percent  $\text{Bi}_2\text{O}_3$  has been added. The theoretical compositions of these two glasses in weight percent of constituent oxides are:

	<u>E 1527</u>	<u>E 1527B</u>
PbO	51.0	35.7
$\text{B}_2\text{O}_3$	8.8	6.2
$\text{SiO}_2$	30.0	21.0
$\text{Al}_2\text{O}_3$	3.1	2.2
CdO	3.1	2.2
$\text{Na}_2\text{O}$	1.5	1.1
$\text{TiO}_2$	2.0	1.4
$\text{ZrO}_2$	1.0	.7
$\text{Bi}_2\text{O}_3$	--	30.0

##### 2. $\theta$ , Substrate and T

$\theta$  is the contact angle of the E 1527 or E 1527B glass, in degrees, measured on the material listed under Substrate at the temperature, in  $^{\circ}\text{C}$ , listed under T. The contact angle measurements on copper (Cu) substrates were conducted in a nitrogen atmosphere, and all other measurements were conducted in air.

##### 3. Time

This column gives the length of time that the glass and substrate had been at temperature T when contact angle  $\theta$  was measured. The entry

"Direct" indicates that the measurement was made after as short a time as possible at temperature.

#### 4. References

- D1. T. T. Hitch and K. R. Bube, "Basic Adhesion Mechanisms in Thick and Thin Films," RCA Laboratories, Final Report for the period January 1, 1975-December 31, 1975, Contract No. N00019-75-C-0145, pp 103-5, 30 January 1976.
- D2. *ibid*, January 1, 1974-December 31, 1974, Contract No. N00019-74-C-0270, pp 210-7, 31 January 1975.

TABLE D1

## Contact Angles

Glass No.	$\theta$	Substrate	T	Time	Reference
E1527	98	Alumina	800	Direct	D1
E1527	55	Alumina	800	100 Sec	D1
E1527	64	Alumina	875	Direct	D1
E1527	35	Alumina	875	100 Sec	D1
E1527	43	Alumina	950	Direct	D1
E1527	20	Alumina	950	100 Sec	D1
E1527	70	Cu	800	Direct	D1
E1527	37	Cu	800	100 Sec	D1
E1527	53	Cu	875	Direct	D1
E1527	25	Cu	875	100 Sec	D1
E1527	24	Cu	950	Direct	D1
E1527	10	Cu	950	100 Sec	D1
E1527	66	Ag	800	Direct	D1
E1527	47	Ag	800	100 Sec	D1
E1527	50	Ag	875	Direct	D1
E1527	32	Ag	875	100 Sec	D1
E1527	38	Ag	950	Direct	D1
E1527	20	Ag	950	100 Sec	D1
E1527	96	Au	800	Direct	D1
E1527	47	Au	800	100 Sec	D1
E1527	50	Au	875	Direct	D1
E1527	33	Au	875	100 Sec	D1
E1527	38	Au	950	Direct	D1
E1527	23	Au	950	100 Sec	D1
E1527	14.5	Alumina	800	10 Min	D2
E1527	9	Alumina	875	10 Min	D2
E1527	12.5	Alumina	950	10 Min	D2
E1527B	28.5	Alumina	800	10 Min	D2
E1527B	2	Alumina	875	10 Min	D2
E1527B	1	Alumina	950	10 Min	D2

TABLE D1 (Continued)

Glass No.	$\theta$	Substrate	T	Time	Reference
E1527	18.5	Au	800	10 Min	D2
E1527	10	Au	875	10 Min	D2
E1527	9	Au	950	10 Min	D2
E1527B	17.5	Au	800	10 Min	D2
E1527B	1	Au	875	10 Min	D2
E1527B	1	Au	950	10 Min	D2